Risk Posed by Anthropogenically Driven Toxic Pollutants in Abu Qir Bay, East Alexandria, Egypt

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List of Abbreviations

Ace	Acenaphthene
Acy	Acenaphthylene
ADI	Acceptable daily intake
AET	Apparent effect threshold
Ant	Anthracene
AQ	Abu Qir
AQD	Abu Qir Drain
AT	Average timing
BaA	Benzo(a)anthracene
BaP	Benzo(a)pyrene
BbF	Benzo(b)fluoranthrene
BghiP	Benzo(ghi)perylene
BkF	Benzo(b)fluoranthrene
BW	Body weight
CDI	Chronic daily intake
Chy	Chrysene
COPC	Contaminant of potential concern
CR	Cancer risk
DDD	Sum of o,p´-DDD and p,p´-DDD
DDE	Sum of o,p´-DDE and p,p´-DDE
DDT	Sum of o,p´-DDT and p,p´-DDT
DDTs	Sum of all the isomers
DibA	Dibenzo(a,h)anthracene
<DL	Below the limit of detection
DLRA	Detailed level risk assessment
dw	Dry weight
ECD	Electron capture detector
ED	Exposure duration
EEC	Extreme effect concentration
Ef	Exposure frequency
EF	Enrichment factor
ELA	Effect level approach
EqP	Equilibrium partitioning
ERA	Ecological risk assessment
ERL	Effect range low
ERM	Effect range medium

Fla	Fluoranthene
Flr	Fluorene
GC	Gas chromatography
GC/MS	Gas chromatography mass spectrometry
GPS	Global positioning system
h	hours
HCBz	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HCHs	Sum of α, β, γ and δ isomers
HEAST	Health effect assessment summary tables
HF	Hydrofluoric acid
HG	Hydride generation
HHRA	Human health risk assessment
HQ	Hazard quotient
I	Intake
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
InP	Indeno[1, 2, 3 (c,d)]pyrene
IR	Ingestion rate
IRIS	Integrated risk information system
Kow	Octanol water partitioning coefficient
LOAEL	Low observed adverse effect level
LOED	Low observed effect dose
LRMA	Logestic regression model approach
MDL	Method detection limit
min	Minute
MSD	Mass selective detector
Na	Not analyzed
NA	Not available
ND	Not detected
NOAEL	No observed adverse effect level
NOED	No observed effect dose
OSF	Oral slope factor
PAHs	Polycyclic aromatic hydrocarbons
PBDE	Polybrominated diethyl ether
PCBs	Polychlorinated biphenyls
PCBz	Pentachlorobenzene
PEC	Probable effect concentration

PEc	Predicted environmental concentration
PEL	Probable effect level
Phn	Phenanthrene
PNEC	Probable no effect concentration
POPs	Persistent organic pollutants
Pyr	Pyrene
Rf	Reduction factor
RfD	Reference dose
RPD	Relative percent deviation
RSD	Relative standard deviation
s	Seconds
SLRA	Screening level risk assessment
SLERA	Screening level ecological risk assessment
SQGs	Sediment quality guidelines
$SnCl_2$	Stannous chloride
TCN	Tetrachloronaphthalene
TEC	Threshold effect concentration
TEL	Threshold effect level
TOC	Total organic carbon
TRVs	Toxicity reference values
TSC	Toxicity screening concentration
TSS	Total suspended solids
ÛCL	Upper confidence level
USEPA	United States Environmental Protection Agency
ww	Wet weight

1. Introduction

1.1. Environmental problems of coastal areas

Economic, environmental and demographic pressures converge sharply in the world's coastal regions, creating a complex situation that presents a multi-dimensional challenge to their effective and sustainable management and governance. Coastal waters are the most productive and biodiverse areas of the seas (90% of the global fish catch comes from coastal waters), the coastal lands are intensely populated (60% of the world's human population lives within 200 km of the coast) and numerous episodic physical events that result from the ocean-atmosphere interface, as well as anthropogenic activities, occur in and impact coastal areas including: tsunamis, hurricanes, harmful algal blooms, oil spills and eutrophication. Also, many of the consequences of global climate change will manifest themselves in the coastal areas (sea-level rise, coastal flooding, coastal erosion, changes in weather patterns, etc). Moreover, the high concentration of stakeholders competing for different uses of the same space often creates conflicts; commercial fishing, artisanal fishing, tourism and recreation, shipping, non-living resource extraction (oil, gas, corals, etc.), aquaculture, industrial and national security interests are all active in the coastal zone. Furthermore, as population and industrialization increase, the economic, environmental and social importance of this area also increases, intensifying the pressures on coastal resources.

Finding equilibrium between these forces is a formidable task. More specifically, the challenges of coastal area management include: distinguishing what is part of the natural variability of coastal ecosystems and climate patterns from what is the response of these systems to human activities, balancing development and economic priorities against environmental issues and long-term sustainability strategies, and understanding the social dynamics that dictate the patterns of human behaviour in different coastal zones. Thus, oceanographers and scientists of many disciplines including social scientists, governments, industry, and society must collaborate in the management of these resources in order to achieve an area where environmental health, quality of life and economic benefit are balanced. This approach to coastal management is called Integrated Coastal Area Management (ICAM), and has been mandated by the United Nations and endorsed by the international community.

Growth is the key characteristic of all urbanization processes. As a consequence of growth land is developed, erosion is accelerated, traffic increases, more waste is produced, and the amount of domestic wastewater increases drastically. These agents of urbanization impose a physical and chemical load to surrounding water bodies, changing the ecosystem and leaving a record of disturbance in the sediments of the water body (Vaalgamaa, 2004).

The quality of the aquatic ecosystem is of great interest to the entire world. The introduction of different waste products into estuaries and seas especially those in industrial and population centres has lead to significant increase in the level of contamination by different pollutants. (Förstner, 1983;

Tessier and Campbell, 1988; Buckley et al. 1995; Islam and Tanaka, 2004). Many classes of chemicals are introduced to the marine environment as a consequence of development. Trace elements, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine and organophosphate pesticides, polychlorinated dibenzo-p-dioxins (PCDD) and furans (PCDF) have been widely detected in the atmosphere, water, soil, sediments, and biota. Concentrations vary worldwide depending on the degree of urbanization.

1.2. Trace metals in the marine environment

Natural environment contaminated by trace metals seems to be a worldwide problem (Nriagu and Pacyna, 1988). This phenomenon is especially significant in estuarine and coastal sediments which usually act as a sink receiving the river derived trace metals from the weathered rocks and anthropogenic sources (Martin and Windom, 1991; Zwokman et al. 1996). It has long been recognized that trace metals in marine environment have a particular significance in the ecotoxicology since they are persistent and can be toxic even in trace amounts. (Langston, 1990; Claisse and Alzien, 1993).
Potential sources of metals in the marine environment include riverine inputs, local runoff, atmospheric deposition, smelting, mining, electroplating and other industrial processes, and transport activities. Local runoff and riverine inputs can carry treated and untreated sewage (Galloway, 1979) and industrial effluents (Gross, 1978). These inputs have been shown to carry high levels of heavy metals in many areas (Helz, 1976).

Many factors affect the distribution of trace metals in the marine environment. Generally, as metals enter a coastal environment, they are transferred to the sediment by various processes, i.e. chemical reactions as adsorption onto particle surfaces and coprecipitation with solid phases (Santschi et al. 1990) and by biological activities. However metals don't necessarily remain bound to sediments, they may be available to benthic fauna (Langston, 1990) or be released to the water column through the sediment re-suspension, the sorption/desorption reactions, the reduction/oxidation reaction and the degradation of organisms (Santschi et al. 1990). These processes could enhance the dissolved concentration of trace metals in the environment and threaten the ecosystem (Förstner, 1983; Tessier and Campbell, 1988).

In sediments, many factors control the concentration of trace metals. Calmano et al. (1988a,b, and 1992) and other authors (Gotoh and Patrick, 1972 and 1974; Khalid et al. 1978; Gambrell et al. 1980; Delaune et al. 1981; Gambrell et al. 1991) have demonstrated the importance of dissolved oxygen, pH, salinity, and sediment redox conditions in the remobilization of heavy metals in marine and fresh water sediments. Other influencing factors include the level of dissolved organic matter in pore waters, geochemical composition of sediments, levels of microbial activity, and conditions of the overlying water.

When evaluating the presence of elements and/or pollutant compound in sediments, attention must be paid to the influence of sample composition on the results especially those referring to the inorganic

fraction. Marine sediments consist of different components and phases including crystalline minerals, carbonates, hydrous metal oxides, and organic substances (Szefer et al. 1995), each of different grain size. For this reason, chemical data are evaluated taking into consideration the textural and compositional characteristics of the sediments.

1.3. Analysis of trace metals in sediments

Metals in sediments are generally considered to be present in the following forms: water soluble, exchangeable, carbonate bound, bound to hydrous metal oxides (as Fe, Mn), bound to organic matter and sulfides, and finally in the crystal lattice of the different minerals composing marine sediments. Many terms have been used to describe metals bound to sediments. Metals that are loosely bound to sediments and can be released back to the water column are known as labile metals. Another name used to describe this fraction is non-detrital metals as they are bound to non-detrital particles (Loring et al. 1985). One more term used to describe this portion is non-residual metals. The other portion that is found inside the lattice of sedimentary minerals is known as residual metals, detrital or non-labile metals, as they can't move back to the overlying water column.

Concentrations of total metals in sediments can be obtained by the digestion of the sediment sample in a mixture of acids to release all metals bound to the different fractions of the sediments. But the determination of total metals will not be useful in environmental pollution assessment studies in a given area as it implies that all forms of a given metal have an equal impact on the environment. Such assumption is clearly untenable (Tessier et al. 1979).

Thus, studying the distribution of trace metals in the various phases of sediment determines their behaviour in the environment, their mobility (Rauret et al. 1988), bioavailability (Szefer et al. 1995; Loring, 1981) and toxicity (Borovec, 1996). Tessier and Campbell, (1987) pointed out that partial extraction of sediment gives a significant insight into the physicochemical factors influencing the bioavailability of trace metals. Trace metal levels for a particular benthic organism have been shown to be related to relatively easily extractable fractions rather than a total metal concentration in the adjacent sediment (Pempkorviak et al.1999), but this may not be the case for other organisms where the accumulation mechanisms are different. Moreover, different metals accumulate in different organs and biota.

Methods for measuring metals in each fraction of the sediment are known as sequential extraction techniques. The results obtained by the sequential extraction technique can provide a wider and deeper insight into the metal pollution in the environment. However, the analytical procedure of the sequential extraction techniques is tedious and time consuming. It is not an effective method, which can be easily applied in environmental investigations (Fang and Hong, 1999; Lin Dong and Deng, 1989).

Numerous extraction schemes for soils and sediments have been discussed in literature (Tessier et al. 1979; Sposito et al. 1982; Wette et al. 1983; Clevenger, 1990; Howard and Vandenbrink, 1999). The procedure of Tessier et al. (1979) is one of the thoroughly researched and widely used procedures to evaluate the possible chemical associations of metals in sediments and soils. Another two important schemes of sequential extraction are those of Kersten and Förstner, (1986) and the Bureau Communautaire de Reference (BCR) sequential extraction method (Ure et al. 1993).

1.4. Persistent organic pollutants (POPs) in the marine environment

POPs that are being introduced into the environment gave rise to concerns at local, national, regional and global scales (UNEP, 1999, 2002) because of their persistence and their resulting effects on the environment. For more than 30 years, awareness has been growing about the dangers posed on human health and the environment by POPs. Many of these substances of greatest concern are organic compounds characterized by persistence in the environment, resistant to degradation and acute and chronic toxicity. In addition, many are subjected to atmospheric, aquatic or biological transport over long distances and are thus globally distributed, detectable even in areas where they have never been used (Bildeman and Olney, 1974; Tanabe et al. 1982; Wade et al. 1988; Iwata et al. 1994; Allen-Gil et al. 1998; Wu et al. 1999). The lipophilic character of these substances causes them to be incorporated and accumulated in the tissues of living organisms leading to body burdens that pose potential risks of adverse health effects. Toxic chemicals which are less persistent but for which there are continuous release resulting in essentially persistent exposure of biota, raise similar concerns.

Due to this concern, the UNEP Governing Council decided in February 1997 (Decision 19/13c) that immediate international action should be initiated to reduce and/or eliminate the emissions and discharges of an initial set of 12 persistent organic pollutants (dirty dozen), a series of negotiations have resulted in the adoption of the Stockholm Convention in 2001. The initial 12 POPs are: aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, hexachlorobenzene, mirex, toxaphene, PCBs, PCDDs and PCDFs. These chemicals have serious health and environmental effects, which may include carcinogenicity, reproductive impairment, developmental and immune system changes, and endocrine disruption thus posing a threat of lowered reproductive success and in extreme cases possible loss of biological diversity (IOMC, 1995). There are, however, numerous other POPs which are also environmental contaminants and are of great concern. Some of them are both persistent and toxic and still in widespread production and use in both industrialized and less industrialized countries (Fu et al. 2003). These include PAHs, HCHs, organotin compounds, organic mercury, endosulfane, atrazine, and polybrominated dipheny ethers (PBDE).

In the aquatic environment, POPs are strongly particle associated due to their hydrophobic properties and tend to be accumulated in sediments. Contaminated sediments may constitute a particular threat

for the associated biota (macrophytes and benthic organisms) and even for other organisms (fish and marine birds) through the marine food web (Gutierrez et al .2007).

PCBs and DDTs are two main categories of POPs present as contaminants in the environment (IPCS, 1993, 1997). Historically, the main reasons for the increased presence of these compounds in the environment are first, the cheap and ready availability of chlorine gas on an industrial scale led to the production of a plethora of chlorinated compounds of technological importance; secondly, many of these polychlorinated organic compounds, cyclic in structure, and highly thermostable, were resistant to biodegradation; and thirdly, the uncontrolled use and discharge of these chemicals resulted in their accumulation and persistence in the environment. PCBs, which had been in industrial use for a much longer time than the organochlorine pesticides, were found to be the major source of organochlorine residues in some environments (Kaiser et al.1985; Albaiges et al. 1987; Ristola et al. 1996; Fernández et al. 1999; Thompson et al. 1999; Vigano et al. 2000; Xu et al. 2000; Strandberg et al .2000; Fox et al. 2001; Jeong et al. 2001; Fu et al. 2003; Christoforidis et al. 2008). Due to their great environmental and health concerns, PCBs and DDTs have been intensively investigated in the last 40 years since they have been discovered as trace levels in environmental samples (Jensen, 1966). Thus, they were the subject of many studies concerning their occurrence in water, sediments and more especially in biota. PCBs are currently followed in pollution monitoring programs like the Reseau National d'Observation de la qualite du milieu marin (R.N.O.) in France (Claisse, 1989; Beliaeff and smith, 1996), or the Mussel Watch in the USA (O'Connor, 2004). Moreover, the physico-chemical properties of the PCB congeners, depending on the number and position of the chlorine atoms bound to the biphenyl structure, make them interesting compounds in order to understand and to model the distribution and fate of organic contaminants in the environment and trophic web (Connolly, 1991; Mackay and Fraser, 2000; Loizeau et al. 2001; Bodin et al. 2007).

PCBs are man-made chemicals and synthesized by substituting variable number of chlorine atoms (from 1 to 10 chlorine atoms) onto the biphenyl aromatic molecular structure to produce 209 congeners. These congeners were manufactured and processed primarily for use as insulating fluids and coolants in electrical equipment and machinery in USA from 1929-1977, with a peak production in the year 1970 about 100,000 tons (Spiro and Stigliani, 1996; USEPA, 1979). PCBs have caused birth defects and cancer in laboratory animals, and they are a suspected cause of cancer and adverse skin and liver effects in humans. USEPA estimates that 150 million pounds of PCB are dispersed throughout the environment, including air and water supplies; an additional 290 million pounds are located in landfills in USA (USEPA, 2000).

PCBs are characterized by high chemical, thermal, and biological stability. In addition they have low vapor pressure, low water solubility, and high dielectric constants. These congeners were used widely as coolant in power transformers, insulators in capacitors, heat transfer fluids, fire resistance, and plasticizers as well as in consumer products such as ink, paper and paints. Due to their wide range of application, high environmental occurrence and high bioaccumulation potentials, they are expected to

spread and accumulate in different environmental compartments. The industrial waste disposal could be the main source of the PCB in the environment.

The toxicity of PCBs depends on their chlorination pattern. A number of PCBs, which have two or more chlorine atoms in the ortho position, express a non-dioxin like toxicity. A smaller group of non ortho and mono ortho substituted congeners elicts similar toxicological effects as 2, 3, 7, 8-TCDD.

Organochlorine insecticides such as DDT, lindane, dieldrin, chlordane, mirex, heptachlor, and heptachlor epoxide are part of wide spectrum of pesticides which are known for their high persistence in the environment. The organochlorine pesticides were banned or restricted since a long time in most of developed countries, but some of them are still used and produced in many developing countries, for instance p,p´DDT and hexachlorocyclohexane (lindane) are still produced in India (Ahmad et al.1996). Pesticides could enter the aquatic environment from agricultural irrigation returns, wash out processes, soil erosion, domestic and industrial waste disposals as well as by direct application to the aquatic environment.

Of all marine pollutants, oil and petroleum hydrocarbons have received the greatest attention due primarily to the highly visible effect of the oil pollution and the lethal effects of oil and petroleum hydrocarbons on marine organisms. Polycyclic aromatic hydrocarbons arise from natural and anthropogenic sources, although the later generally predominate (Law and Biscaya, 1994). Natural sources of PAHs include forest and prairie fires (Blumer and Youngblood, 1975), natural petroleum seeps, post-depositional transformations of biogenic precursors over relatively short period of time (Wakeham et al. 1980), whereas anthropogenic sources include: combustion of fossil fuel (Hites et al. 1977; Tolosa et al. 2004), long range atmospheric transport of PAHs adsorbed onto soot or airborne particulate matter (Lunde and Bjorseth, 1977; Laflamme and Hites 1978; Tolosa et al. 2004), urban runoff containing PAHs derived from abrasion of street asphalt and automobile tires and vehicle emissions (Wakeham et al.1980) and spillage of petroleum and its refined products which contain complex assemblages of PAHs (Boehm et al. 1991). PAHs may be introduced or produced diagenetically during the evolution of organic matter in sediments (Benlaken et al. 1997) and from the short-term degradation of biogenic precursors (Baumard et al. 1998a).

Carcinogenic activity is closely related to PAHs structure (high molecular weight PAHs). Some related heterocyclic compounds (those containing S such as benzothiophenes and dibenzothiophenes) may also cause taint in commercially exploited fish and shellfish rendering them unfit for sale. Polycyclic aromatic hydrocarbons are group of compounds with different structures ranging from 2-ring structure to 6-ring structure. The molecular weight increases by increasing the number of aromatic rings. There are marked differences in behaviour of PAHs in aquatic environment between low molecular weight compounds (naphthalene) and the high molecular weight compounds as benzo[ghi]perylene as a consequence of their different physio-chemical properties, in particular their water solubility.

Once PAHs are released, they are subjected to a variety of changes as a result of microbial degradation, photooxidation and chemical oxidation (Readman et al. 1982), even so, most PAHs are persistent both in the aqueous phase and in sediments.

The highest concentrations of PAHs in sediments are expected to be found in estuaries, harbours and in coastal areas receiving industrial and urban discharges. PAHs incorporated in sediments may have limited bioavilability and the presence of high concentrations of PAHs doesn't necessarily imply a biological effect (Knutzen, 1995; Paine et al. 1996).

Polycyclic aromatic hydrocarbons (PAHs) in sediments are mainly associated with organic matter (Neff, 1979; Knejovich et al. 1987) and PAHs sediment content depends on grain size distribution (Law and Andrulewiez, 1983; Readman et al. 1984; Raoux and Garrigues, 1993). Fine grain sized sediments have been shown to accumulate PAHs at greater concentrations than coarser sands (Law and Andrulewiez, 1983).

For certain PCBs but particularly for some PAHs, metabolic reactions lead to the synthesis of highly reactive diol and epoxy derivatives, which may bind to proteins, DNA and other endogenous molecules, and cause deleterious effects and be responsible for genotoxicity (Varanasi, 1989; Sole et al. 2000).

Surfacial sediments are considered the ultimate sink for many classes of anthropogenic contaminants. During the last decades, environmental regulation has resulted in a reduction in the loading of waste from terrestrial sources. As sediments integrate pollutant loads over time, the distribution in coastal sediments allow the recognition of major inputs as well as the evaluation of their magnitude and area of influence. The presence of organochlorine compounds in stable level of concentrations in sediment reservoir could act as a non-point source, and has the potential to release the in-place contaminants causing adverse effects to organisms and to human health through trophic transfer and sustain aqueous contamination for a few years should their usage cease (Hong et al. 1995).

1.5. Bivalves in marine environmental studies

The use of sentinel organisms to measure the levels of bioavailable contaminants has been established by various pollution monitoring programs (Goldberg et al. 1978; Phillips, 1980**;** Farrington et al. 1987; Walker and Livingstone, 1992; Claisse et al. 1992; Baumard et al. 1998 b, c; Tanabe, 2000). Mussels and to a lesser extent oysters, which are water-filtering bivalves, have been mainly employed (Farrington et al. 1983). Mussels have been shown to concentrate many organic contaminants by a factor of 10 above the ambient sea water levels and even higher than sediments, providing a direct representation of pollutant bioavailability (Bergen et al. 1993; Thompson et al. 1999). Although bivalves are filter feeders, they are also exposed to the sediments, especially sediment dwelling bivalves (Dame, 1996). Exposure of organisms to pollution depends on water turbidity (Foster et al. 1987; Pruell et al. 1987), location of the organism in the water column (Roesizadi et al. 1978)

and on feeding modes (Bjorseth et al. 1979; Swartz et al. 1990; Porte and Albaiges, 1993; Hickey et al. 1995).

Phillips, (1980); Gosling, (1992) and Farrington and Trip, (1995) have explained many of the advantages in using molluscs, especially bivalves as bioindicators of contaminant loads in coastal and estuarine systems:

1) Species of bivalves such as mussels and oysters are having a wide geographical distribution and are dominant members of estuarine and coastal communities. Since the same species of bivalves can be collected from wide geographic locations, the problems in comparing data obtained from different species are eliminated. This will be an important parameter especially in tropical areas with a wide biodiversity.

2) They are sedentary, and are therefore, better than mobile species like fin fishes as integrators of chemical contamination in a given area.

3) They are relatively tolerant to a wide range of environmental conditions such as salinity, season, sampling position in the water column, size, reproductive condition etc. Since these animals are sedentary, most of the problems that may arise due to these variables can be relatively simply eliminated during the sampling procedure (Phillips, 1980).

4) Bivalves are relatively tolerant to a wide range of environmental contaminants, including moderately high levels of many types of contaminants. They can exist in habitats contaminated by variety of pollutants at the same time.

5) Many bivalves are reasonably long-lived and so specimens of various sizes (year-classes) can be sampled easily for comparison.

6) Bivalves are suspension feeders (filter-feeders) that pump several liters of water every hour and concentrate many chemicals in their tissues, by factors of 10 to 10^5, relative to the concentrations in water. This makes the measurement of contaminants easier.

7) In comparison with many other animals in the same trophic level, bivalves have a very low level metabolizing enzyme activities of organic contaminants. Therefore, the contaminant concentrations in the tissues of bivalves more accurately reflect the magnitude of environmental contamination.

8) Most of them are of commercial interest and a measure of chemical contaminants in them is of public interest.

1.6. Environmental risk assessment

The field of risk assessment was developed in the 1980s, in recognition of the need to evaluate the effects of human activities at the ecosystem level and to incorporate this ecological information into regulatory decisions. Typically, risk assessment involves two components: an assessment of risk, followed by attempts to minimize unacceptable risks based on that assessment. These two components have been formalized in risk assessment into, respectively, the scientific process of human and ecological risk assessment and the separate process of risk management (Campbell et al. 2006)

While there are many definitions of the word risk, the United States Environmental Protection Agency (USEPA) considers risk to be the chance of harmful effects to human health or to ecological systems resulting from exposure to an environmental stressor. A stressor is any physical, chemical, or biological entity that can induce an adverse response. Stressors may adversely affect specific natural resources or entire ecosystems, including plants and animals, as well as the environment with which they interact (USEPA, 1992).

Risk assessment can be classified into ecological risk assessment (ERA) and human health risk assessment (HHRA). HHRA has always been concerned with one species and with protection of all individuals of that species. The ERA is concerned with many species. Except for threatened and endangered species, the goal of ERA is the protection not of individuals but rather of populations and communities (Campbell et al. 2006). The realization that industrial chemicals could be hazardous outside the laboratory or factory resulted in the development of HHRA. The USEPA began developing guidelines for HHRA in 1970s. Development of similar guidelines for ERA began in the 1980s (USEPA, 1992).

Risk assessment characterize the nature and magnitude of health risks to humans (e.g., residents, workers, recreational visitors) and ecological receptors (e.g., birds, fish, wildlife) from chemical contaminants and other stressors, that may be present in the environment. Risk managers use this information to help them decide how to protect humans and the environment from stressors or contaminants. Risk assessment is, to the highest extent possible, a scientific process. In general terms, risk depends on the following factors:

1) Concentration of a chemical in an environmental medium (e.g., soil, water, air),

2) Contact (exposure) frequency of a person or ecological receptor with the contaminated environmental medium, and

3) The inherent toxicity of the chemical.

Following a planning and scoping stage where the purpose and scope of a risk assessment is decided, the risk assessment process usually begins by collecting measurements that characterize the nature and extent of chemical contamination in the environment, as well as information needed to predict how the contaminants behave in the future. Based on this, the risk assessor evaluates the frequency and magnitude of human and ecological exposures that may occur as a consequence of contact with the contaminated medium, both now and in the future. This evaluation of exposure is then combined with information on the inherent toxicity of the chemical (that is, the expected response to a given level of exposure) to predict the probability, nature, and magnitude of the adverse health affect that may occur. In an ideal world, all risk assessments would be based on a very strong knowledge base (i.e., reliable and complete data on the nature and extent of contamination, fate and transport processes, the magnitude and frequency of human and ecological exposure, and the inherent toxicity of all of the chemicals). However, in real life, information is usually limited on one or more of these key data needed for risk assessment calculations. This means that risk assessors often have to make estimates and use judgment when performing risk calculations, and consequently all risk estimates are uncertain to some degree. For this reason, a key part of all good risk assessments is a fair and open presentation of the uncertainties in the calculations and a characterization of how reliable (or how unreliable) the resulting risk estimates really are. In the face of uncertainty, conservative assumptions are used to ensure that risks are not underestimated (i.e., to minimize the likelihood of false-negative results). Developing a risk assessment is often an iterative process, which involves researchers identifying and filling data gaps in order to develop a more refined assessment of the risk. This in turn may influence the need for risk assessors and risk managers to refine the scope of the risk assessment further triggering the need for more data or new assumptions.

The USEPA established a framework (**Figure 1**) for assessing ecological and human health risk (USEPA, 1989; USEPA, 1992; USEPA, 1997a, b; USEPA, 1998) that was intended to provide a clear and rigorous approach to the estimation of effects associated with uncontrolled release of toxic substances. Both the USEPA, (1997a; 1998) and the Wisconsin Department of Natural Resources (WDNR), (1992) have issued basically compatible guidance for conducting ecological risk assessments. The approach for the ecological screening level risk assessment (SLRA) for Abu Qir Bay in the present study followed these established frameworks and guidelines for assessing the ecological risks.

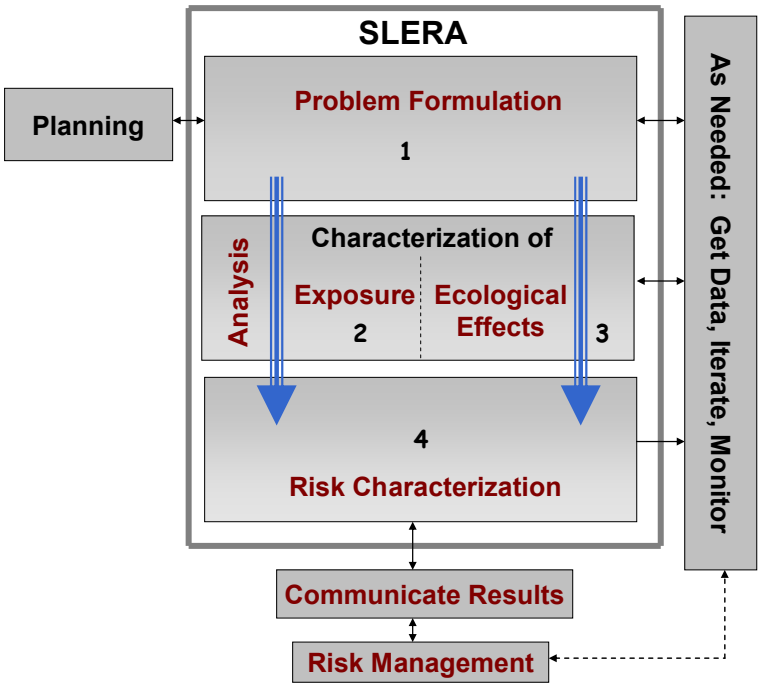


Figure 1: Steps of the ecological risk assessment as proposed by the USEPA.

All ERAs typically involve four main phases:

1) ***Problem formulation***: Systematic planning and information gathering phase, geared towards determining the overall scope and objectives of the ERA (**Figure 2a**).

2) ***Exposure assessment***: Data gathering and analysis phase geared towards quantifying relevant exposure concentrations for ecological resources of concern at a site (**Figure 2b**).

3) ***Effects assessment***: Data gathering and analysis phase focussed on determining exposure concentrations or rates not associated with adverse ecological effects, or focussed on actually characterizing the presence or absence of adverse effects to ecological resources at a site (**Figure 2b**).

4) ***Risk characterization***: Assimilation phase which integrates the results of the effects and exposure assessments to characterize risks to the receptors (**Figure 2c**). There are a variety of terms used to classify various ERA tiers; the most commonly used is a two-tier system: screening-level risk assessment (SLRA) and detailed-level risk assessment (DLRA). In most cases, the risk assessment process starts with the screening level to determine contaminants of potential concern followed by the more detailed, site specific risk assessment process (DDRA). Differences between both tiers are shown in **Table 1**.

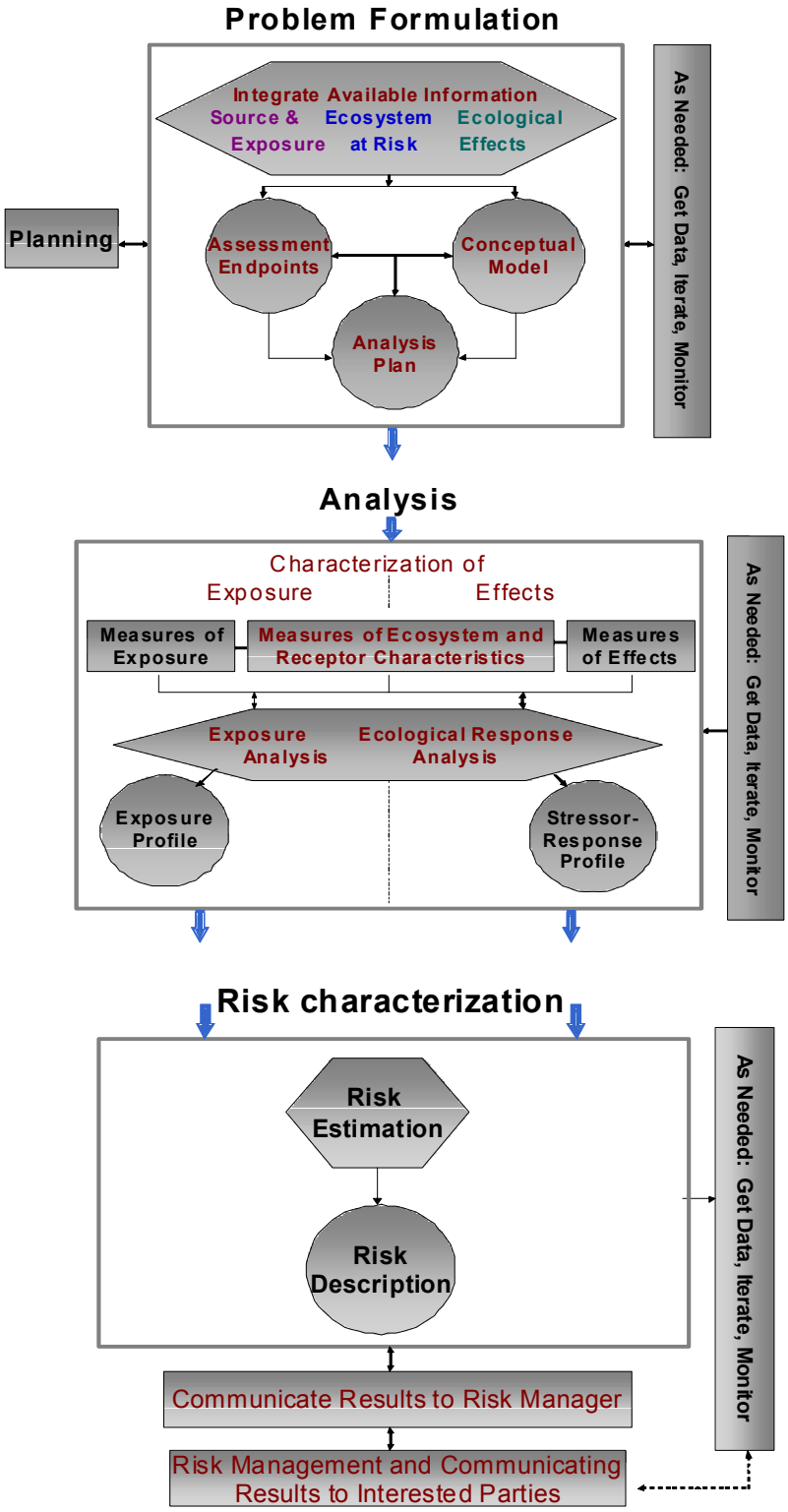


Figure 2: Detailed steps of the ERA as proposed by USEPA.

Table 1: Generic difference between SLRA and DLRA (Hill et al. 2000).

Parameter	SLRA	DLRA
Information used	Available	New information
Level of effort	Generally relatively low	Generally relatively high
Level of conservatism	High (over protective; no effects level)	Decreased (attempts to be reasonably protective; low effects level)
Stressors and receptors considered	All possible	Focused subset
Level of uncertainty	High	Decreased (degree depends on risk management objectives and other factors)
Uncertainty assessment	Point estimates only	Typically a probabilistic assessment
HQs/TRVs	Generic only	Site specific (exposure effects relationships may be determined)
Extrapolation	Broad	Limited
Effects estimation	Primarily individuals	Populations/communities
Multiple lines of evidence	Possible preliminary consideration	Detailed consideration

HQ: Hazard quotient TRVs: Toxicity reference values

SLRAs are intended to identify which stressors (e.g., contaminants) pose potentially unacceptable risks and which can be ruled out from further analysis. This can be done in the risk characterization step, where a comparison is made between the predicted (or measured) environmental concentration (PEc) of the contaminant and its predicted (or measured) no effect concentration (PNEC). This ratio is referred to as the HQ:

$$HQ = \frac{\text{Predicted (estimated) environmental concentration (PEc)}}{\text{Predicted no effect concentration (PNEC)}}$$

If the predicted effect concentration and/or the predicted no effect concentration are based on generic rather than site specific information, then the calculated HQ will only provides an indication of hazard. In such a case, if the HQ < 1, there is negligible risk, and if HQ > 1, there is a possibility of risk but not the certainty of risk.

Because of the high level of conservatism in a SLRA (if done properly), the fact that a substance is 'screened in' following an SLRA does not necessarily indicate a real risk. Conversely, the manner in which a substance is `screened out' convincingly indicates lack of risk.

The simplest risk assessment may be based on ambient concentrations of contaminants. For example, if we are interested in assessing potential ecological risks to sediment biota from sediment contamination, we could start by measuring contaminant concentrations in sediment and comparing those to appropriate sediment quality values (Chapman and Mann, 1999; Chapman et al. 1999). In

this case, the HQ approach is suitable. If the HQ<1 (i.e., if measured concentrations are less than sediment quality values, we assume there is no potential for unacceptable risks).

In the SLRA stage, it is rare that effects benchmarks are derived from site-specific data. Instead, SLRAs typically rely on effects data derived from literature sources or data collected from other sites. This lack of site-specificity typically requires that conservative assumptions be made in the effects assessment to ensure that site-specific risks are not underestimated. However, best professional judgement is often required to ensure that the level of conservatism is not so extreme that it cascades' throughout the SLRA, rendering the outcome meaningless due to over-conservatism. The effect of multiple conservative assumptions on risk estimates can be significant (Finkel, 1989; Burmaster and Harris, 1993; Bogen, 1994).

A SLRA can involve extrapolations between different classes of organisms (e.g., chicken data applied to all avian receptors). However, the reality is that physiological differences between taxonomic classes can be large, thus unless these differences are known, such extrapolations are often questionable. A DLRA attempts to minimize such extrapolations, i.e., limiting the difference between extrapolations over taxonomic distances or between dissimilar taxa (e.g., emphasizes similarities in physiology, behaviour, body mass). Where data limitations make extrapolations a necessity, a DLRA will provide a more thorough evaluation of the implications for risk estimation (e.g., by assessing the sensitivity of risk estimates to different interpretations of the data).

1.7. Study area

The selected area of study known as Abu Qir Bay, is a semicircular shallow basin lying at 35 km to the east of Alexandria city between Abu Qir Peninsula (west) and the Rosetta branch of the Nile (east), with a shoreline about 50 km long. It lies between 30^{o} 4$^{'}$- 30^{o} 21$^{'}$ East and 31^{o} 16$^{'}$-31^{o} 30$^{'}$ North (**Figure 3**). The bay is relatively shallow with a depth ranging from less than one meter along the coast, increasing gradually away from the shore to reach a maximum depth of about 15 m (Nasr et al. 2004).The bay has a surface area of about 360 km^2, its mean depth is 12 m and the volume of water is about 4.32 km^3. The amount of freshwater discharged into the bay is estimated as 2130 x 10^6 m^3/y (Abdel-Moati, 2001). The mean concentrations of hydrographic parameters, nutrients and metals recorded in the bay waters are shown in **Table 2**.

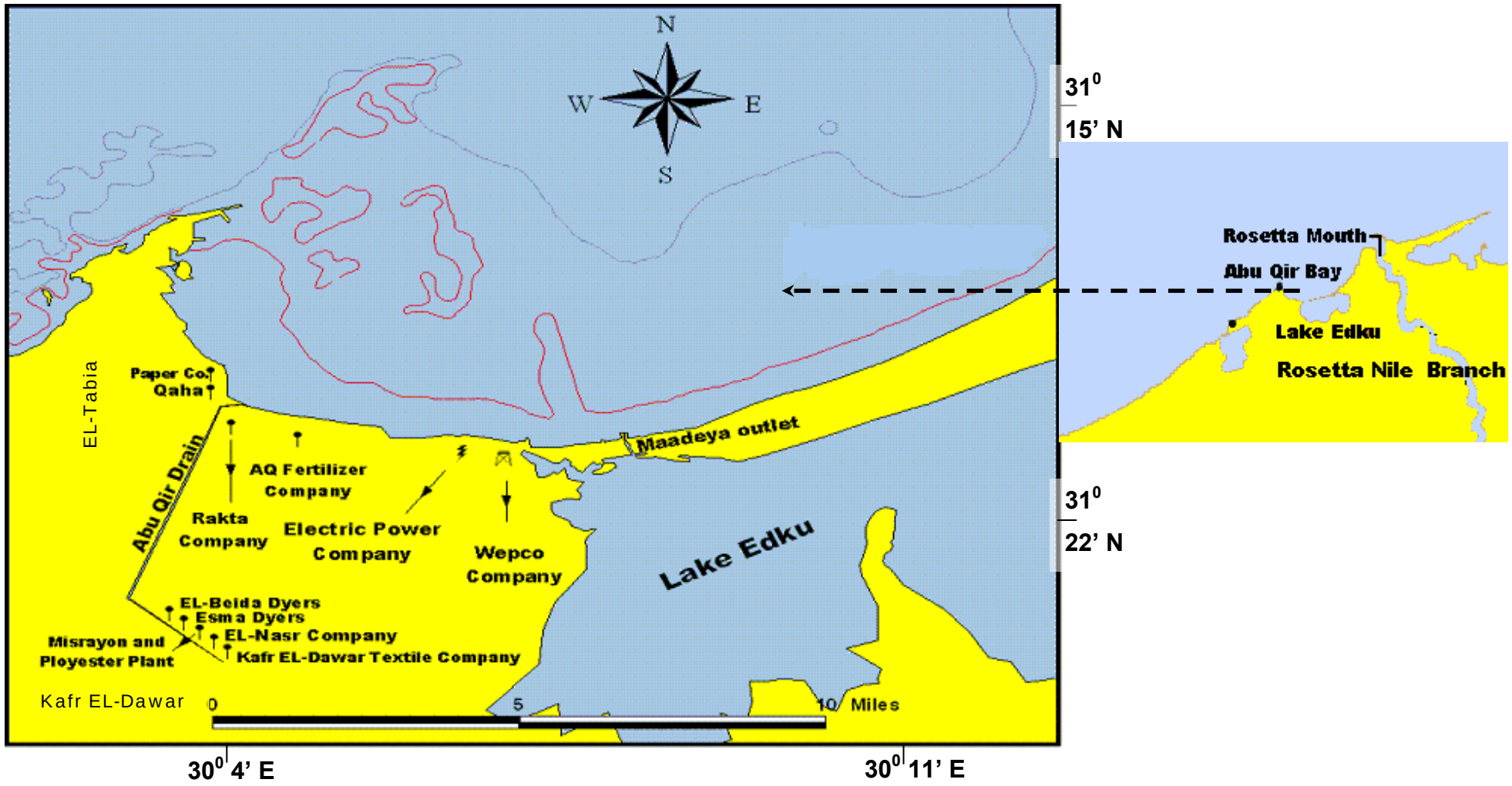


Figure 3: Map of Abu Qir Bay, Egypt.

Table 2: Mean concentrations of physicochemical parameters, nutrients and metals of water from Abu Qir Bay (Abdel-Moati, 2001).

Parameter	Value
pH	8.05
Dissolved oxygen (DO) (ml/L)	4.93
BOD_5 (mg/L)	16.2
Salinity (psu)	28.4
Total suspended matter (TSM) (mg/L)	35.5
Chlorophyll a (µg/L)	3.32
Dissolved inorganic phosphorus (DIP) (µm/L)	1.11
NO_3^- (µm/L)	5.87
NH_4^+ (µm/L)	3.00
Pb (µg/L)	1.48
Cd (µg/L)	1.15
Hg (µg/L)	1.47

Abu Qir Bay was considered one of the most profitable fishing areas before it was assumed polluted by the disposal of sewage and industrial effluents. It receives different types of pollutants, and could be considered as the main source of pollution in the whole area. The Main sources of pollution are: Abu Qir Drain (AQD), Lake Edku and Rosetta Branch of the River Nile in the eastern part of the bay (**Table 3**) (Sharaf EL-Din et al. 1980; Saad et al. 1980).

Table 3: Pollution sources in Abu Qir Bay.

Source	Types of pollution, (ASRT, 1984)	Rate of Discharge
Abu Qir Drain	Food processing and canning, paper industry, fertilizers industry and textiles manufacturing and agricultural effluents.	1.5-2 million m^3/day, (ASRT, 1984)
Maadeya outlet of Edku Lagoon	Drainage water from agriculture discharged into Lake Edku	1.5-2 million m^3/day, (Wahby and EL-Deeb, 1982)
Rosetta branch of the River Nile	Discharged Nile water that carries agricultural waste from cultivated lands in the delta region.	2-5 x 10^9 m^3/year, (El-Hehyawi, 1984)

Abu Qir Drain receives and discharges industrial wastewaters from 22 different factories (Gerges, 1980; Said et al .1995) of food processing and canning, paper industry, fertilizer industry, and textile manufacturing (EL-Metwally, 1977; Aboul Dahab, 1989 and Abdelmoneim and shata, 1993). Besides, 15000 m^3/day of industrial wastes are discharged directly into the bay (Masoud, 2005). The hydraulic and pollution loads are shown in **Table 4**. The major industrial activities affecting the quality of Abu Qir Bay are located in EL-Tabia and Kafr EL-Dawar regions (**Figure 3**). The hydraulic pollution loads from both regions are represented in **Figure 4**. The contribution of industrial effluents in Abu Qir Drain is shown in **Figure 5**. In addition, brackish water is drained into the bay via AQD from the vast cultivated

land of the north-eastern part of the Delta (Gerges, 1980; Wahby and EL-Deeb, 1982; Aboul-Naga et al. 2002).

Table 4: Characterization of industrial wastewater discharged to Abu Qir Bay (directly and through Abu Qir Drain) (Abdel-Moati, 2001 and Masoud, 2005).

Parameter	Direct	Through AQD	Total
pH	--	7.9±0.4	--
Flow, m^3/d	15000	132300	147300
Suspended solids (S.S), t/d	11	106	117
COD, t/d	52	70	122
BOD, t/d	13	26	39
Oil and grease, t/d	0.09	1	1.09
NH_3, t/d	0.68	0.07	0.75
DIP (µm/L)	--	2.8±2.8	--
Pb (µg/L)	--	5.3±2.6	--
Cd (µg/L)	--	9.3±7.8	--
Hg (µg/L)	--	80±30	--
Total heavy metals, t/d	0.01	0.96	0.97

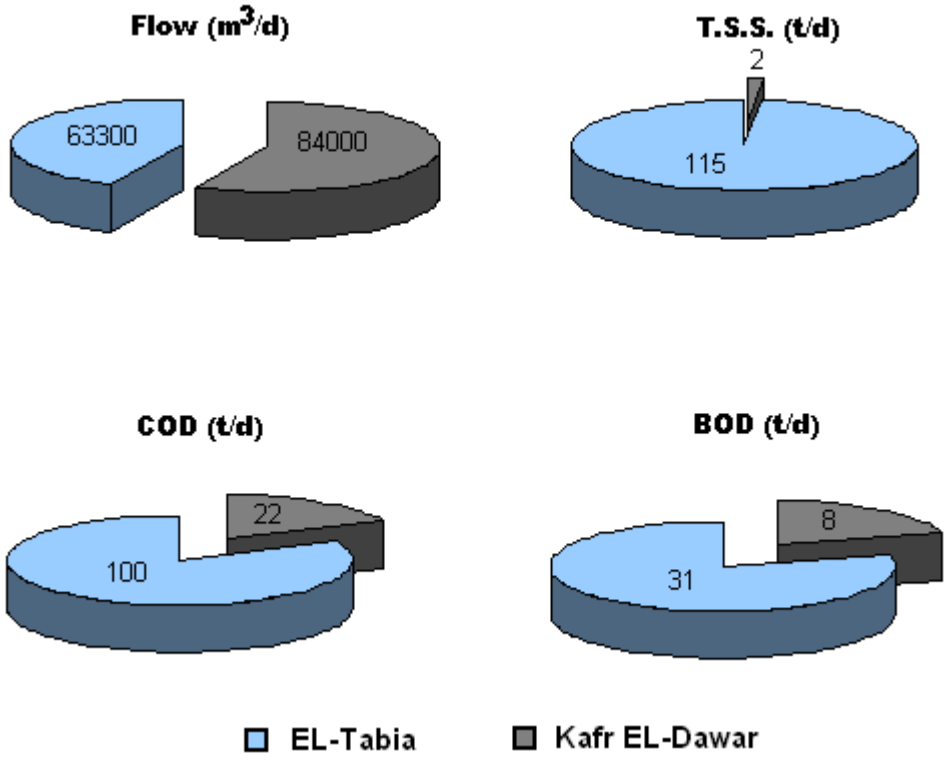


Figure 4: Contributions of the industrial areas to the flowrate, total suspended solids (T.S.S.), COD and BOD in Abu Qir Bay. (Masoud, 2005).

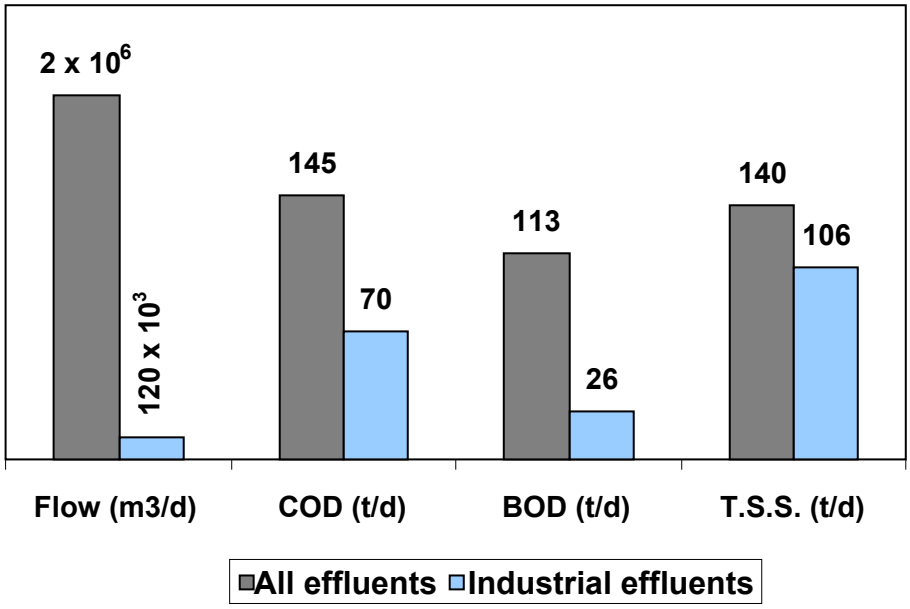


Figure 5: Contribution of industrial effluents from the total amount of effluents.

It was obvious that the industrial wastewaters discharged from EL-Tabia region were more polluted than that of Kafr EL-Dawar region (**Figure 4**) and that although the amount of water discharged from Kafr EL-Dawar region is larger, COD, BOD and total suspended solids were much higher in the industrial wastewaters of EL-Tabia and thus greatly influence the environmental quality of Abu Qir Bay. It was also clear that the industrial effluents were responsible for the elevated levels of BOD, COD and T.S.S. although the industrial flowrate represented only a small portion of the total flowrate into Abu Qir Bay (**Figure 5**).

Lake Edku, the second major source of pollution in the bay discharges agricultural drainage water through the Maadeya Outlet (**Table 3**). This is a shallow channel with an average depth of about 3 m and an average width of 20 m. The annual average of the drainage water discharged into the lake is about 1 x 10^9 m^3 (EL-Sayed et al. 1993). In the past, different types and quantities of pesticides were found in this water (Gerges, 1980). Average concentrations of nutrients and metals in water discharged from Lake Edku are given in **Table 5**. The level of pollution by agricultural run-off in Abu Qir Bay is largely dependent on the nature and magnitude of the water exchange with Lake Edku, which is apparently of considerable magnitude in summer and autumn season and is rather limited in winter (Gerges, 1980).

At the northeast extremity, the bay receives considerable quantities of freshwater from the River Nile. This water carries important quantities of suspended sediments and greatly influences the physico-chemical characteristics of the bay water.

Table 5: Average concentrations of nutrients and metals in water discharged from Lake Edku into Abu Qir Bay (Abdel-Moati, 2001).

Variable	Lake Edku
pH	8.22±0.2
TSM (mg/L)	87±43
DIP (µm/L)	4.12±3.1
NO_3^- (µm/L)	28.8±22
NH_4^+ (µm/L)	17.8±9.6
Pb (µg/L)	3.8±1.6
Cd (µg/L)	4.3±2.9
Hg (µg/L)	20±6

Due to the land runoff of freshwater from Rosetta mouth and brackish water from Lake Edku, the water salinity in Abu Qir Bay varies with a wide range. This wide range of salinity variation causes a significant variation in water density. Therefore density currents take a considerable contribution of water circulation in the bay. Alam EL-Din and AL-Hogaraty, (2001) studied the water circulation resulting from density variations of the bay waters by using a three dimensional hydro-dynamic model to simulate the thermocline circulation in Abu Qir Bay during the different seasons with a horizontal resolution of about 0.5 min. The simulation results showed that the density (thermohaline) circulation in the bay is very complicated. A lot of rotating motions (eddies) can be detected during different seasons. The main features of the water circulation during winter are the extensive anticlockwise eddy in front of Rosetta mouth due to the huge amount of freshwater discharged during this season.

During the spring, the general trend of surface circulation is dominated by the clockwise direction. The brackish water discharged from Lake Edku directed north-westward to the open sea in the western part of the bay, while the Mediterranean water enters the bay in the central and the northern parts. The maximum current speed of about 13 cm/s can be detected in the western part of the bay in front of EL-Maadeya outlet (**Figure 3**).

In summer, the general pattern of the surface circulation is characterized by the seaward flow in front of Maadeya Outlet and the shoreward flow in the central and the western parts of the bay. This circulation pattern leads to the accumulation of less saline water in the eastern and western part of the bay.

During autumn, the shoreward flow of Maadeya outlets divided the brackish water discharged from Lake Edku and Tabia Pumping station into two parts: the first part flows in the north-western direction causing an accumulation of less saline water along the south-western coasts. The second one flows north-eastward making a clockwise motion in the central part of the bay, where the less saline water accumulated inside the bay.

1.8. Previous studies on Abu Qir Bay

Studies on the environmental state of Abu Qir Bay have concentrated in the past mostly on simple chemical and bulk analysis of sediments (Saad et al. 1980; Aboul Dahab, 1988; Aboul Dahab, 1989; Abdel Moneim and Shata, 1993; EL-Sokkary, 1993; Aboul-Naga et al. 2002 and Abdel-Fatah, 2006) and no published data are available for Se, As, Co and Hg. The most comprehensive study on the trace metals pollution in sediments of the bay was performed by EL-Sokkary, (1993) more than a decade ago. Few studies on the status of persistent organic contaminants in the bay sediments have been conducted (Abd-Allah, 1992; Abd-Allah and Abbas, 1994; EL-Nemr et al. 2007)

Some surveys have been carried out in the Nile estuaries and the Mediterranean coastal waters near Alexandria including Abu Qir Bay investigating the trace organic pollutants. No monitoring studies have been conducted on mirex, toxaphene, chlordane, endosulfane and PAHs. For aldrin, dieldrin, endrin and heptachlor, data are very limited (Barakat, 2004). Aldrin (10-70 ng/L), dieldrin (<0.1-5 ng/L), heptachlor (3-44 ng/L) and endrin (<0.1-53 ng/L) concentrations were determined in seawater (dissolved + particulate) of Abu Qir Bay and EL-Mex Bay, with higher concentrations reported in Abu Qir Bay (Abd-Allah and Abbas, 1994). Aldrin, dieldrin and heptachlor levels (dissolved + particulate) in the seawater of Alexandria Coast ranged between 0.2 and 6 ng/L (Abd-Allah, 1999). PCBs (31-872 ng/L as Aroclor 1242), DDTs (17-166 ng/L) concentrations were detected in seawaters of Abu Qir Bay (Abd-Allah, 1992). HCBz (2-25 ng/L), PCBs (20-844 ng/L as Aroclor 1260) and lindane (<0.1-60 ng/L) concentrations were also reported in Abu Qir Bay sweaters (Abd-Allah and Abbas, 1994). In the period from 1997 to 1998, HCBz (30 ng/L), DDTs (78 ng/L), PCBs (310 ng/L as Aroclor 1260) and lindane (310 ng/L) concentrations were detected in Lake Edku Output. HCBz (37 ng/L), DDTs (61 ng/L), PCBs (420 ng/L as Aroclor 1260 and 520 ng/L as Aroclor 1254), and lindane (410 ng/L) were also detected in Abu Qir Drain effluents in the same period (Abbassy, 2000).

Mean concentrations of cyclodiene pesticides (aldrin, endrin, heptachlor and heptachlor epoxide), DDTs, lindane, HCBz, and PCBs in different coastal and freshwater sediments are presented in **Figure 6**. Total concentrations of cyclodiene pesticides have been reported in sediments collected in 1988 from the Nile River and ranged from below the detection limit to 2917 µg/kg dw, with a decreasing abundance in the order aldrin > heptachlor > endrin (EL-Gindy et al. 1991). Concentrations of aldrin (13-72 µg/kg dw), dieldrin (<0.1-5 µg/kg dw), endrin (<0.1-56 µg/kg dw) and heptachlor (11-45 µg/kg dw) were reported in sediment samples from Abu Qir Bay and EL-Mex Bay (Abd-Allah and Abbas, 1994). Higher levels were reported in Abu Qir Bay.

Trace metals were reported in fish species (Emara, 1982; EL-Nabawy et al. 1987a and Mohamed and Khaled, 2007), algal species (Mohamed and Khaled, 2007) and bivalve species from Abu Qir Bay. As for bivalves, *Donax trunculus* was greatly investigated in the bay (Khalid, 1997; Ahdy, 1999; Abdel Moati, 2002; EL-Sikaily et al .2004). *Mytilus* spp. was investigated in one old study (Abdel Moati, 1991). *Mactra corallina* was investigated in two studies (EL-Rayis et al. 1997; Ahdy, 1999).

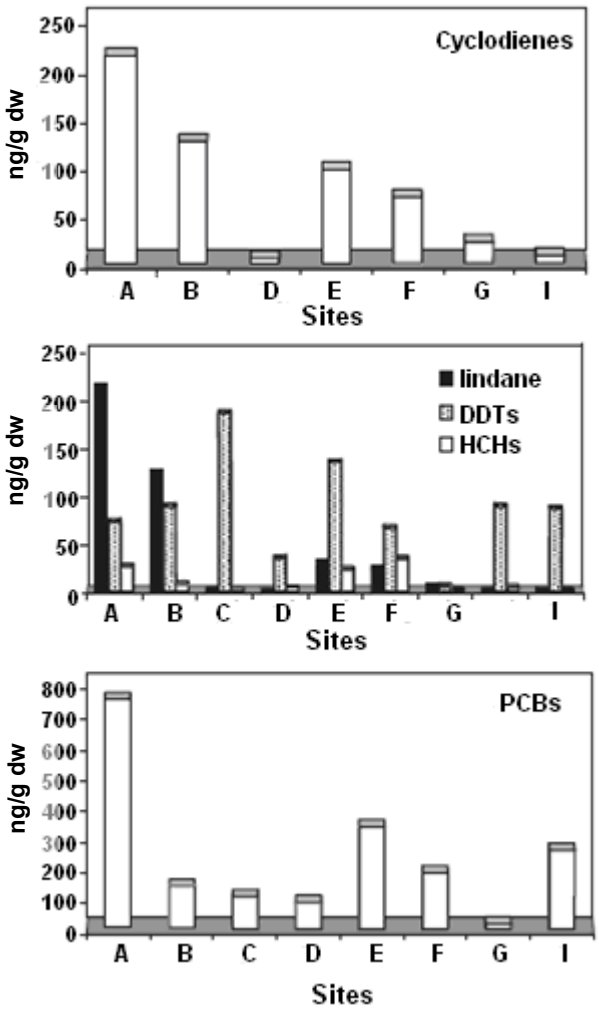


Figure 6: **Mean concentrations of persistent organic pollutants in sediments from different locations in Egypt (Barakat, 2004). (A): River Nile, Rosetta branch (EL-Gindy et al. 1991); (B): River Nile, Damietta branch (EL-Gindy et al. 1991); (C): Lake Manzala (Yamashita et al. 2000); (D): Lake Maryut (Barakat et al. unpublished data); (E): Abu Qir Bay (Abd-Allah, 1992; Abd-Allah and Abbas, 1994); (F): EL-Mex Bay Abd-Allah, 1992; Abd-Allah and Abbas, 1994); (G): Off Nile Delta (Abd-Allah et al. 1992; Abbas et al. 1991); (H): Alexandria Harbour (Barakat et al. 2002); (I): River Nile, Cairo (Yamashita et al. 2000). PCBs levels are reported as Aroclor 1242 for sites A, B, E, F and G and as ΣPCBs for sites D and H.**

In most cases, As, Cr and Se were completely ignored and only Cd, Cu and Pb were investigated in *Mactra corallina*.

Few studies investigated the concentrations of hydrophobic organic compounds in tissues of marine organisms (fish and bivalves) in Abu Qir Bay (EL-Nabawi et al. 1987b; Abd-Allah et al. 1998; EL-Deeb et al. 2007). Fish species were more intensively investigated compared to the bivalves, where only *Donax trunculus* was examined. Cyclodiene pesticides have been determined during the past 30 years in a large number of fish in coastal areas in Egypt. Concentrations were in the range (<0.1-25 µg/kg ww) (Abd-Allah et al. 1990, 1998; Abd-Allah and Ali, 1994; EL-Nabawi et al. 1987b).

Low levels (<2 µg/kg ww) were detected in *Donax* sp. From Gamasa, Abu Qir Bay and Damietta (Abd-Allah et al.1998). DDT concentrations in the range 39-160 µg/kg ww were reported in fish from Abu Qir Bay and EL-Mex Bay (EL-Nabawi et al. 1987b; Abd-Allah and Ali, 1994). DDTs were detected in the range 6.8-30 µg/kg ww in *Donax trunculus* sampled from Abu Qir Bay (Abd-Allah et al. 1998). At all locations, p,p'-DDE was the predominant isomer.

PCBs were the second most predominant contaminants occurring in fish samples indicating that they are ubiquitous contaminants in the coastal marine environment of Egypt. High concentrations in the range 180–227 µg/kg ww (reported as Aroclor 1248) and 26–90 µg/kg ww (S6 congeners) were found in fish samples from El-Max (Abd-Allah and Ali, 1994) and Abu-Quir (El Nabawi et al. 1987b), respectively. Aroclor 1248 levels were reported in the range 17–31 µg/kg ww in fish (*M. cephalus*) and 19–46 µg/kg ww in bivalves (*Donax* sp.) from coastal areas in Egypt (Abd-Allah et al. 1998).

1.9. Objectives of the present work

As reported in the previous section, most of the data available on the concentrations of different toxic pollutants in the bay are more than a decade old. But, industrial, agricultural and human activities in and around Abu Qir Bay have increased dramatically in the last 20 years and updated data are needed as the basis for decision makers for an establishment of effective management plans. Chemical industry is by far the main source of hazardous wastes in the developed regions. Frequent problems have been faced by these industries in disposing of the hazardous waste they generate. In addition to the industrial effluents, pollution in the bay results from agricultural pesticides, raw sewage, and urban effluents. The need for better environmental protection in Egypt and threats to the health of the Egyptian citizens have made environmental protection in the last years more a government priority. Thus, Egypt has stipulated the necessity for land management strategies, environmental sound agricultural practices and ameliorated irrigated and drainage systems; regulations of fertilizers, pesticides and mineral usage and development of agricultural legislation in harmony with an effective environmental policy. Regulation and protection of the environment in Egypt comes under the jurisdiction of the Ministry of the Environment, the Ministry of Agriculture, Livestock, Fisheries and Land Reclamation (Barakat, 2004).

In 1994, Egypt passed the Environmental Protection Law, providing the foundation for Egypt's environmental protection efforts. The Egyptian Environmental Affairs Agency (EEAA) was created to formulate environmental policies, develop, undertake, oversee environmental protection efforts and promote environmental education in Egypt. After all these efforts, monitoring of the environmental quality is of great importance to determine the order of effectiveness of all the adopted governmental steps and to determine if further steps are required to improve the quality of the environment. Thus the objectives of the present study were set as follows:

1) Determination of the concentrations and spatial distribution of persistent pollutants (organochlorines and metals) in surfacial sediments of Abu Qir Bay.

2) Quantification of the selected pollutants in tissues of benthic organisms (two bivalve species: *Mactra corallina and Tapes decussata*) to assess pollutants bioaccumulation in the bay.

3) Determination of the factors influencing the distribution of the selected pollutants in the bay sediments.

4) Comparison between the obtained concentrations in the present study with previous studies performed on Abu Qir Bay to evaluate the present environmental quality of the bay.

5) Evaluation of the extent to which pollutants in sediments of Abu Qir Bay can pose risk to benthic fauna (bivalves) by performing a screening-level ecological risk assessment process to objectively rank the risks of individual pollutants.

6) Evaluation of the possibility of occurrence of human health effects from the ingestion of the bivalve tissues by performing human health risk assessment.

7) Characterization of the spatial variability of risk and to determine whether risk hotspots exist.

8) Establishment of applicable recommendations for protection and management of the bay based on the obtained results from the risk assessment process.

2. Materials and Methods

2.1. Sampling

Surfacial sediment samples were collected at 30 different locations in Abu Qir Bay during February-April 2006 using an Ekman grab sampler. In addition, mussel samples from 13 locations were collected during the same period representing two different species: *Mactra corallina* and *Tapes decussata*. *Mactra corallina* was collected from 7 different locations in front of the Maadeya Outlet, the Wepco Petroleum Company and between the Electric Power Plant and the Fertilizer Company, whereas *Tapes decussata* was collected from the western part of the bay. The mussels were collected by the help of the scuba diver. Sampling sites are shown in **Figure 7**. The location of each sampling site was determined using a GPS (Trimble Navigation). Sampling sites were chosen according to the main sources of pollution in the bay. A nearshore-offshore profile was sampled in front of each of the main sources of pollution in the area and samples also included areas away from the influence of anthropogenic activities near the open sea (Stations 5, 6 and 7)

The pH was measured directly after collection of the samples using a pH meter (Corning Glass Workers, Model 3). Each sediment sample was then divided into two parts; one was stored in a glass jar for the analysis of organic pollutants and the other part in a plastic jar for the inorganic analysis. Mussel samples from each location were washed with seawater and also divided into two halves. They were stored in an ice box over ice until transferred to the central lab of the Department of Environmental Sciences, Faculty of Science, Alexandria University. Afterwards, samples were stored frozen at –20 ^{o}C until analysis. The coordinates of each sampling site together with the measured values of pH and water depth are presented in **Appendix I, Table A1**.

2.2. Reagents and chemicals

The used reference standards are given in **Table 6**. Stock solutions were prepared for each individual organic target pollutant with a concentration of 1 µg/µL either in n-hexane or in n-hexane/toluene. Chemical substances and organic solvents used are given in **Table 7**.

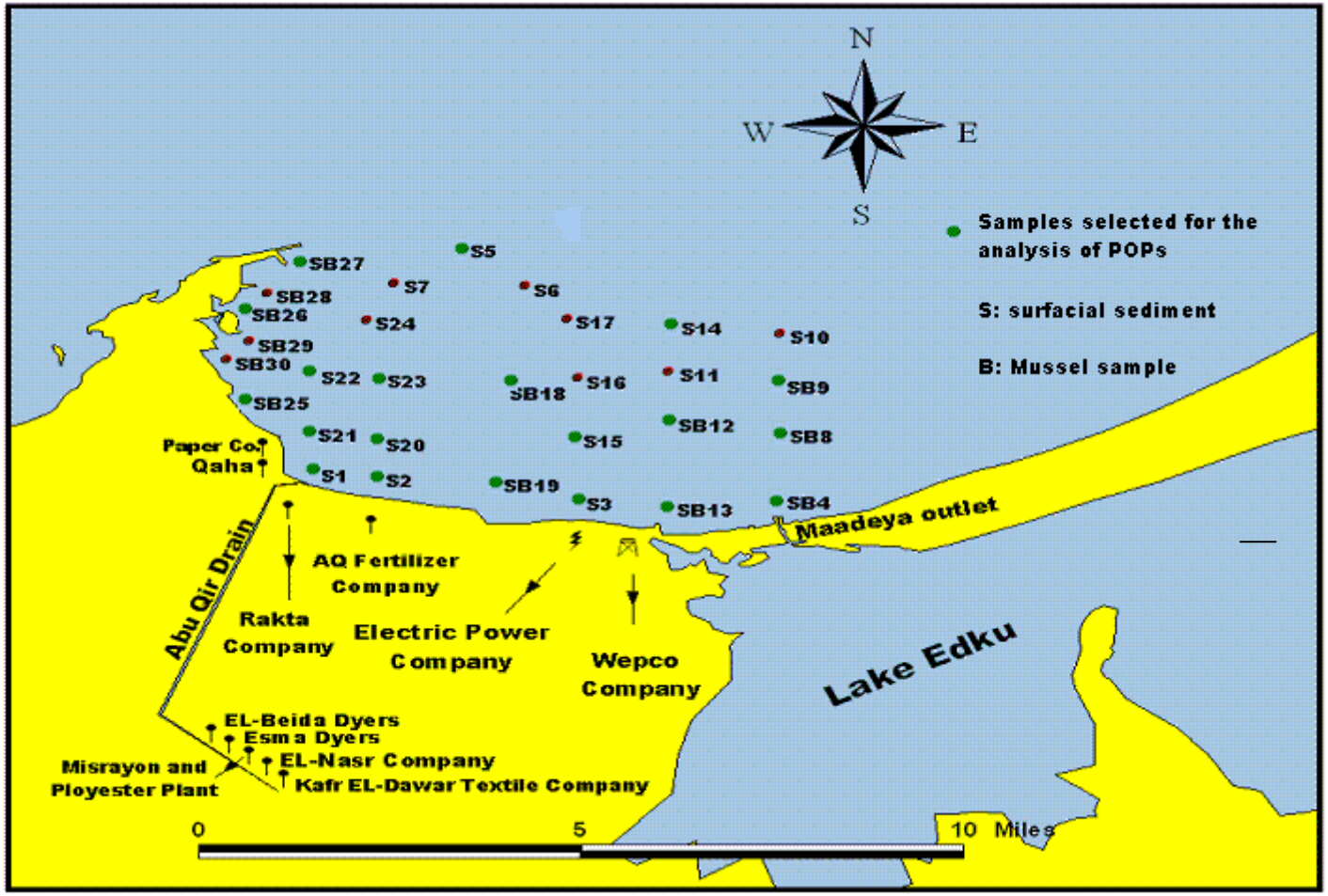


Figure 7: Location of sampling sites in Abu Qir Bay.

Table 6: Organic and inorganic reference standards.

Reference substance	Abbreviation	Company
PCB 28 (Purity > 99.9%)		Promochem, Germany
PCB 52 (Purity > 99.7%)		Promochem, Germany
PCB 70 (Purity > 99.7%)		Promochem, Germany
PCB 101 (Purity > 99.8%)		Promochem, Germany
PCB 118 (not mentioned)		Promochem, Germany
PCB 153 (Purity > 99.8%)		Promochem, Germany
PCB 138 (Purity > 99.5%)		Promochem, Germany
PCB 126 (not mentioned)		Promochem, Germany
PCB 156 (not mentioned)		Promochem, Germany
PCB 180 (Purity > 99.6%)		Promochem, Germany
PCB 169 (not mentioned)		Promochem, Germany
Pentachlorobenzene (> 99%)	PCBz	Riedel-de Haen, Germany
Hexachlorobenzene (> 99%)	HCBz	Riedel-de Haen, Germany
α-Hexachlorocyclohexane (97.8%)	α-HCH	Dr. Ehrenstorfer, Germany
β-Hexachlorocyclohexane (99.5%)	β -HCH	Dr. Ehrenstorfer, Germany
γ-Hexachlorocyclohexane (99.1%)	γ -HCH	Dr. Ehrenstorfer, Germany
δ-Hexachlorocyclohexane (98.4%)	δ -HCH	Dr. Ehrenstorfer, Germany
Heptachlor (>99.0%)		Riedel-de Haen, Germany
Aldrin (98.1%)		Dr. Ehrenstorfer, Germany
Chlorpyrifos (99.7%)		Dr. Ehrenstorfer, Germany
Cis-Heptachlor epoxide (10 ng/µL)	cis Epoxide	Dr. Ehrenstorfer, Germany
trans-Heptachlor epoxide (10 ng/µL)	trans Epoxide	Dr. Ehrenstorfer, Germany
trans-Chlordane (> 99.4%) cis-Chlordane (> 99.4%)		Institute of Organic and Industrial Chemistry, Poland
o,p´-DDE (99.9%)		Dr. Ehrenstorfer, Germany
o,p´-DDD (99.6%)		Dr. Ehrenstorfer, Germany
o,p´-DDT (99.9%)		Dr. Ehrenstorfer, Germany
p,p´-DDE (99.9%)		Dr. Ehrenstorfer, Germany
p,p´-DDD (98.8%)		Dr. Ehrenstorfer, Germany
p,p´-DDT (98.4%)		Dr. Ehrenstorfer, Germany
Dieldrin (98.5%)		Dr. Ehrenstorfer, Germany
α-Endosulfane (99.4%)		Dr. Ehrenstorfer, Germany
β-Endosulfane (99.4%)		Dr. Ehrenstorfer, Germany
Methoxychlor (>99.0%)		Riedel-de Haen, Germany
Mirex (99.0%)		Dr. Ehrenstorfer, Germany
USEPA 16 PAH (100 ng/µL)		Promochem, Germany
1,2,3,4-Tetrachloronaphthalene	1,2,3,4-TCN	Promochem, Germany
Single element plasma standard solutions in 5% HNO_3 (1000 and 10000 mg/L)		Alfa Aesar, Germany

Table 7: Chemical substances and solvents.

Chemical substance	Abbreviation	Company
Salts		
Anhydrous sodium sulfate (>98%)	Na_2SO_4	ROTH GmbH, Germany
Ammonium acetate (p.a.)	CH_3COONH_4	Riedel-de Haen, Germany
Sodium hexametaphosphate	Calgon	Merk, Germany
Sodium acetate (> 99%)	CH_3COONa	Fluka, Switzerland
Sodium chloride (99.5%)	NaCl	ROTH GmbH, Germany
Ammonium oxalate (p.a.)	$(NH_4)_2OCOCOO$	Merck, Germany
Ascorbic acid (p.a.)		Merck, Germany
Urea (p.a.)		Merck, Germany
Potassium iodide (p.a.)	KI	Merck, Germany
Potassium hydroxide (> 85%)	KOH	ROTH GmbH, Germany
Sodium hydroxide (p.a.)	NaOH	Merck, Germany
Stannous chloride (p.a.)	$SnCl_2$	Merck, Germany
Sodium borohydride (p.a. >96%)	$NaBH_4$	Fluka, Switzerland
Calcium carbonate (p.a. >99%)	$CaCO_3$	Fluka, Switzerland
Oxalic acid	$H_2C_2O_6$	Fluka, Switzerland
Acids		
Hydrochloric acid (37% p.a.)	HCl	Riedel-de Haen, Germany
Nitric acid (65% p.a.)	HNO_3	Merck, Germany
Hydrofluoric acid (40% extrapure)	HF	Merck, Germany
Indicators		
Phenolphthalein indicator		Merck, Germany
Adsorbents		
Aluminium oxide 90 active neutral (70-230 mesh)	Alumina	Merck, Germany
Silica gel 60 (70-230 mesh)		Merck, Germany
Others		
Sea sand (extra pure)		ROTH GmbH, Germany
Copper powder (99.0%)	Cu	Fluka, Switzerland
Hydrogen peroxide (30% p.a.)	H_2O_2	ROTH GmbH, Germany
Solvents		
Acetone (pesticide grade)		Merck, Germany
n-hexane (pesticide grade)		Merck, Germany
Ethyl acetate (pesticide grade)		Merck, Germany
Methanol (pesticide grade)		Merck, Germany

2.3. Physicochemical characterization of sediments

2.3.1. Sediment grain size analysis

Sediment grain size analysis was performed according to Sweet et al. (1998). Approximately 20 g of each sample were placed in a large glass jar. This sample size was chosen to minimize the interaction of individual grains with each other during settling and lessening the probability of flocculation. The sample was treated with approximately 50 to 100 mL of 30 % hydrogen peroxide (volume varies with the organic matter content of the sample) for 12 h prior to analysis in order to oxidize the organic matter present. Afterwards, the sample was washed with distilled water (about 100 mL) to remove soluble salts. Then 400 mL of sodium hexametaphosphate solution (2.5 g/L) were added to disperse the particles in the sample, and the samples were stirred by a dispersing system (Ultra-Turrax T25, Omnilab, Germany) for approximately 24 h.

A stainless steel sieve (mesh size, 63 µm) was placed over a 1-L graduated cylinder. The hexametaphosphate solution containing the dispersed sediment was poured over the sieve and washed with dispersant to rinse any remaining fine-grained sediment into the cylinder. This process separated the gravel/sand fraction (on the sieve) from the silt/clay fraction (in the cylinder). The coarse fraction was washed into a pre-weighed beaker with distilled water and placed in an oven (100 - 130 °C) to be dried. The beaker was removed from the oven and left to cool to room temperature. The beaker was then weighed with the sand/gravel fraction to 0.1 mg.

The volume of liquid in the graduated cylinder containing the silt/clay material was taken to exactly one liter volume with dispersant solution. The cylinder was stirred vigorously and left to stand for 1 h. When no flocculation of particles was observed, analyses continued. If flocculation of particles was observed, the sample was discarded and the procedure was restarted with a new sample. Afterwards, the cylinder was stirred vigorously starting at the bottom and working up until all the sediment was distributed uniformly throughout the cylinder. The pipette was inserted to a depth of 20 cm, and at the end of exactly 20 s, 20 mL was withdrawn that represented the silt + clay fraction. The suspension was pipetted into a preweighed beaker. The pipette was rinsed with 20 mL of distilled water and the rinse water was added to the same beaker.

After exactly 2 h and 3 min, a 20 mL aliquot at a depth of 10 cm was withdrawn representing the clay fraction. The aliquot of the suspension was pipetted into a second pre-weighed beaker, rinsed with 20 mL of distilled water and added to the beaker

The beakers were placed in an oven and the suspensions evaporated to dryness for at least 24 h at 100 to 130 °C. After 24 h, the beakers were removed from the oven and left to cool to room temperature. The beakers were weighed to 0.1 mg.

The silt + clay and clay dry weight aliquots included the weight of the added dispersant. The weight of the dispersant was then subtracted from the two withdrawn fractions and the total amount of both fractions in 1 L was calculated by multiplication with 50. The sample weight of the silt fraction was calculated by subtracting the sample weight of the clay fraction from the sample weight of the silt + clay fraction.

$$\text{Total dry mass} = m(\text{sand}) + m(\text{silt}) + m(\text{clay})$$

Where "m (sand)" is the sum of the sand and gravel fractions (particles greater than 63 µm).

2.3.2. Determination of the water content

Water content was determined by calculating the difference between the weight of a sample before and after drying in an oven at 105 ^{0}C for 24 hours.

2.3.3. Determination of total organic carbon (TOC)

About 5 g of each dry, ground (agate grinder) sediment sample was treated with 10 to 25 ml of 12.5 % HCl, until the cessation of bubbling. The treated sediment samples were filtered on a pre-weighed filter paper and washed well with double deionized water to remove the excess of acid completely. The filter paper was then placed in an aluminum tray and dried in an oven over night at 80 ^{0}C. After complete dryness, samples were reweighed, ground and 5 to 20 mg aliquot of each sample was analyzed for TOC using DC-90 Total Organic Carbon Analyzer (Dohrmann, USA). It was operated at 800 ^{0}C and coupled to an infrared gas analyzer for detection of CO_2. The measurement range was from 0 to 2500 mg/L. The system worked under HP-PEAK 96 data operating and management software. The calibration curve was prepared using a mixture of oxalic acid with alumina ($H_2C_2O_4$/ Al_2O_3) in a ratio of (1:9) ranging from 100 to 500 µg carbon.

2.3.4. Determination of calcium carbonate

Total carbonate content of the sediment samples was determined by titration technique (Herrin, 1957 and Black, 1965). About 1 g of each sample was treated with 30 mL of standardized HCl (c = 0.5 mol/L) and the released amount of CO_2 was determined by back titration with previously standardized NaOH (c = 0.25 mol/L) solution using phenolphthalein indicator.

2.4. Determination of total metals in sediments

2.4.1. Sample preparation

Total metals were determined according to EPA method 3052 (EPA, 1996a), with some modifications. Sediment samples were oven dried at 40 ^{0}C for almost a week. After drying, sediments were ground with an agate grinder and stored in a plastic vial until analysis**.** Sediments were digested using microwave (star*-system, MHS-product, Germany) assisted acid digestion technique. At the beginning, the method had to be optimized until a complete digestion was reached. Different trials together with the optimum method are shown in **Table 8**. After cooling, the HF was sucked from the digested samples using a distillation unit (flexVac condensation/absorption unit, VAC1000, MLS-product, Germany) in the microwave. This technique was checked by using a standard mixture of trace elements that was treated the same way as the samples. After distillation of HF, samples were diluted to 20 ml with 10 % HNO_3 and stored in plastic vials until measurement. For each 8 samples, a blank was run, which was treated the same manner as samples.

2.4.2. ICP-OES analysis

Digested samples were analyzed for trace elements using an ICP-OES (Vista-MPX, CCD simultaneous radial ICP-OES) from Varian, Germany. The device measured each element at 5 different wavelengths. Selected wavelengths (with the lowest interference) for the investigated metals are shown in **Table 9**. To reduce the matrix effect, samples were diluted before measurement. A standard addition method was used for Cd as the detected concentrations of Cd were very close to the detection limit. Therefore, samples were spiked with 1 mg/L Cd standard. Operating conditions for the

device are given in **Table 10**. For every working day, a calibration curve ranging from 0.01 to 100 mg/l including 0.05, 0.2, 1, 5 and 10 mg/L standards was prepared for the investigated metals. A solution of 10 % HNO_3 was used as zero standard. Standards with different concentrations (1 to 10 mg/l) were run every 10 samples to check the stability of the device. When the RSD (%) was less than or equal 10, no recalibration was needed. In the present work, RSD (%) for the standard checks of all metals were below 10 %. 10 % HNO_3 was used as the washing solution after each measured sample.

Table 8: Different digestion experiments applied to the sediments for optimization of the method.

Trials	Acid mixture	Microwave temperature program	Sample weight (g)
Trial 1: EPA (3052)	3 mL HF + 9 mL HNO_3	1 min to 75 ^{0}C, then 4 min to reach to 185 ^{0}C and finally remain at this temperature for 10 min	0.2- 0.5
Trial 2	6 mL HF + 6 mL HNO_3 + 2 mL HCl	1 min to 75 ^{0}C, then 9 min to reach to 200 ^{0}C and finally remain at this temperature for 20 min	0.2- 0.5
Trial 3	6 mL HF + 6 mL HNO_3 + 2 mL HCl	1 min to 75 ^{0}C, then 9 min to reach to 185 ^{0}C and finally remain at this temperature for 50 min	0.2- 0.5
Trial 4	6 mL HF + 6 mL HNO_3 + 2 mL HCl	1 min to 75 ^{0}C, then 9 min to reach to 185 ^{0}C and remain at this temperature for 50 min, the ramp to 200 ^{0}C in 5 min and remain at this temperature for 55 min	0.2- 0.5
Optimum method	8 mL HF + 3 mL HNO_3 + 2 mL HCl	1 min to 75 ^{0}C, then 4 min to reach to 185 ^{0}C and remain at this temperature for 13 min, the ramp to 200 ^{0}C in 5 min and remain at this temperature for 25 min	0.2-0.5

Table 9: Selected wavelengths (nm) for ICP-OES.

Element		Wave length (nm)
Al	I	936.152
Mn	II	259.372
Fe	II	238.20
V	II	268.796
Cr	II	267.716
Co	II	230.786
Ni	II	227.021
Cu	I	327.395
Zn	I	213.857
As	I	188.980
Se	I	196.026
Cd	I	228.802
Sn	II	181.059
Hg	II	194.164
Pb	II	220.353

I: atomic emission line
II: ion emission line

Table 10: Optimized working conditions for the ICP-OES.

Power (kw)	1.2
Argon flow (L/min)	15
Auxiliary argon flow (L/min)	1.5
Neublizer pressure (kpa)	255
Plasma view	Radial
Viewing height (mm)	10
Replicate readtime (s)	20
Instrument stabilization delay (s)	45
Sample uptake delay (s)	30
Pump rate (rpm)	20
Rinse time (s)	10
Replicates	3
Neublizer	V-groove
Spray chamber	Sturman-Masters

For the determination of As, Se and Hg the sensitivity of the ICP-OES was not high enough in order to detect them directly. Thus, As and Se were measured using the vapour generation accessory VGA-77 (Varian, Germany) connected to the ICP-OES. Each element was measured in a separate run. Prior to the measurement, As and Se had to be reduced to the arsenite and selenite forms respectively.

For As, a pre-reduction step was performed by mixing 5 ml of the previously digested sample with 2.5 ml of KI solution and 2.5 ml HCl (37 %). The mixture was left for 15 minutes to complete the reduction process. The mixture was then measured directly by the VGA-77-ICP-OES system.

For Se, 5 ml of the previously digested sample was added to 30 ml of concentrated HCl. The mixture was immersed in a boiling water bath for about 30 minutes (to ensure the complete reduction of Se). The samples were then removed from the water bath, and left for a while to cool. When they reached to a warm temperature, 1 ml of 20 % (w/v) urea was added for degassing. Samples were left to further cool and during this period, they were shaken occasionally for degassing. After cooling, each sample was poured in a 50 ml measuring flask and filled up to the mark with deionized distilled water.

In the hydride generation unit, reduced forms of As and Se were mixed with $NaBH_4$ (0.3 % in 0.05 % NaOH) and HCl and were converted to arsenohydride and selenohydride. Argon gas was used to remove the arsenohydrides and selenohydrides from the solution and introduce them into the plasma torch. $NaBH_4$ solutions for the flow injection system were prepared daily by dissolving appropriate amounts of powdered $NaBH_4$ in NaOH solution. The solution was filtered before use.

The selected wavelengths for As and Se are listed in **Table 9**. A calibration curve was prepared for each element ranging from 1 µg/L to 30 µg/L. A standard was run each 10 samples to check for the stability of the conditions. The optimized working conditions of HG-ICP-OES for As and Se measurements are shown in **Table 11**.

Table 11: Optimized working conditions for the HG-ICP-OES (As and Se).

Plasma	
Power (kw)	1
Plasma gas (L/min)	15
Auxiliary gas (L/min)	1.5
Nebulizer pressure (kPa)	240
Instrument stabilization time (s)	60
Sample delay time (s)	50
Pump rate (rpm)	25
Plasma view	lrRadi
Fast pump flow	off
Hydride generation	
HCl acidity of the sample for As	3.0 mol/L
HCl acidity of the sample for eS	7.2 mol/L
Carrier gas pressure	3.5 bar

Hg was measured by the same VGA-77 unit using the cold vapour technique according to Varian application note number 36. Hg was reduced using 25 % (W/V) $SnCl_2$ dissolved in concentrated HCl. Hg was measured directly without any further preparations. The optimum conditions are shown in **Table 12**. The selected wavelength for Hg was 194.164 nm. A calibration curve was prepared for Hg ranging from 20 µg/L to 100 µg/L.

Table 12: Optimized working conditions for the HG-ICP-OES (Hg).

Power (kw)	0.9
Plasma gas (L/min)	13.5
Auxiliary gas (L/min)	1.5
Nebulizer pressure (kPa)	240
Instrument stabilization time (s)	60
Sample delay time (s)	50
Pump rate (rpm)	25
Fast pump operation	off

2.5. Sequential extraction procedures for trace metals in the sediments

Trace metals were sequentially extracted from the bay sediments according to the method of Förstner and Calmano, (1982) and Zeien, (1995). Sub-samples of the homogenized dry sediment, equivalent to 1 g were weighed into clean dry glass jars (250 mL) and sequentially leached with the reagents and conditions specified in **Table 13**. After the completion of each stage (1-4), each sample was filtered through a 0.2 µm cellulose acetate filter. The filtered solution was stored in a plastic vial until analysis.

Table 13: Reagents and conditions employed in the sequential extraction procedure.

Metal fraction	Extraction reagent	Extraction conditions
Exchangeable (F1)	20 mL of 1 M $C_2H_7NO_2$ adjusted to pH 7 with NH_3	Shake at room temperature for 2 h
Carbonate bound (F2)	20 mL of 1 M $C_2H3NaO_2 \cdot 3H_2O$ adjusted to pH 5 with HOAc	Shake at room temperature for 5 h
Reducible (F3)	100 mL of 0.2 M $(NH_4)_2C_2O_4 \cdot H_2O$/ $C_2H_2O_4 \cdot 2H_2O$ adjusted to pH 3 with NH_4OH	Shake at room temperature for 24 h
Oxidizable (F4)	1) 30 mL of H_2O_2 (30%) 2) 100 mL of 0.2 M $(NH_4)_2C_2O_4 \cdot H_2O$/ $C_2H_2O_4 \cdot 2H_2O$ adjusted to pH 3 with NH_4OH	Place on a hot plate at 80 ^{0}C till dryness and left to cool Shaken at room temperature for 24 h

The residual fraction was calculated by subtracting all fractions of the sequential extraction from the total metal concentration.

Each fraction was measured with the ICP-OES using procedures described in section 2.4.2, but the calibration standards were diluted with the respective extracting reagent.

2.6. Determination of total metals in mussels

2.6.1. Sample preparation

Mussel tissues were removed from the shells (20 g representing 20-30 individuals), pooled and dried in an oven at 40 ^{0}C for about one week. Afterwards the dry mass and the water content were calculated.

Samples were digested in a microwave (star*-system, MHS, Germany) and analyzed for As, Cd, Cr, Cu, Hg, Mn, Pb, Se and Zn using an acid mixture composed of 8 mL HNO_3 (65 % p.a. grade, Merck, Darmstadt, Germany) and 2 mL H_2O_2 (30 % p.a. grade, Carl Roth, Karlsruhe, Germany). Samples were soaked in the acid mixture overnight to release gases. A temperature program was developed in this study that allowed the digestion of 1 g of each dry ground sample. The microwave temperature program was adjusted as follows: 2 min to reach to 75 ^{0}C at a power of 700 W, 4 min to reach to 100 ^{0}C at a power of 800 W, 10 min to reach to 150 ^{0}C at a power of 900 W, 10 min to reach to 200 ^{0}C at a power of 900 W and finally samples were left at 200 ^{0}C for 12 minutes at a power of 1000 W. A blank was run with each sample batch. 20 % of the total number of samples were analyzed as replicates in order to check for the reproducibility of the results.

2.6.2. ICP-MS analysis

Digested samples were analyzed for trace metals (except Hg) using an ICP-MS (Micromass Platform, New jersey, USA). The plasma was run with an incident power of 1,400 kW. Data were obtained by the peak hopping method with 5 sweeps per reading and a dwell time of 2 to 4 s. Including the pre-integration time (30 s) and 5 replicates of the measurements, the analyses time for one sample totals to 2.5 min. In order to avoid argon interferences, the MS was equipped with a hydrogen rinsed gas

collision cell. Measurements were corrected for blank values by the instrument software. The calibration ranges of the trace metals, together with the selected masses for quantitation purpose are summarized in **Table 14**.

Hg was measured with the same procedure applied for sediments as mentioned above (section 2.4.2.).

Table 14: Calibration range (µg/L) and the quantitation masses for the metals measured by ICP-MS.

Element	Calibration range (µg/L)	Monitored masses
As	0-50	^{75}As
Cd	0-10	$^{112/114}Cd$
Cr	0-50	^{52}Cr
Cu	0-50	^{63}Cu
Mn	0-500	^{55}Mn
Pb	0-20	$^{206/208}Pb$
Se	0-50	^{80}Se
Zn	0-200	^{66}Zn

2.7. Determination of organic pollutants in sediments

2.7.1. Extraction

Sediment samples were extracted according to Batarseh, (2003). Homogenized wet sediment samples (60 to 80 g) were ground and mixed with 70 to 90 g anhydrous sodium sulphate (previously muffled at 500 ^{0}C for 4 h) and 70 g sea sand in a porcelain mortar until a flowing powder was obtained. This mixture was then dry packed in a glass column (5 cm i.d x 50 cm) over a piece of glass wool and 10 g Na_2SO_4. Each sample was eluted with 450 mL n-hexane/acetone (2:1 v/v) over night at a flow rate of 1 mL/min. Finally, the extract was rotary evaporated and the solvent was exchanged with n-hexane. The extract was brought to a final volume of 1 mL under a gentle stream of nitrogen.

2.7.2. Cleanup with column chromatography

Sediment extracts were cleaned up using column chromatography according to Kolb et al. (1995) with some modifications. A chromatographic column (2 cm i.d. x 30 cm) was plugged with a piece of glass wool, filled with n-hexane and packed with 10 g alumina (90 neutral, 70-230 mesh previously activated at 185 ^{0}C over night and deactivated with 12.5 % water afterwards) topped with 2 cm Na_2SO_4.The alumina column was conditioned with about 25 mL n-hexane. Afterwards the target compounds were eluted with 100 mL n-hexane/ethyl acetate (7:3). Finally, the eluate was evaporated and the solvent was exchanged with n-hexane and brought to a final volume of 1 mL under a gentle stream of nitrogen.

Sediment extracts were further cleaned up using a silica gel (60, 70-230 mesh) chromatographic column (2 cm i.d. x 30 cm). 10 g of activated silica gel (activated at 185 ^{0}C over night) were slurry packed in the column with n-hexane. The silica gel was topped with 1 cm layer of Na_2SO_4. After conditioning, the extract was quantitatively added to the top of the column and the glass vial was washed with 2 mL of n-hexane which were also added to the top of the column. The target compounds were eluted into two fractions: the first fraction (F1), that included the PCBs, PCBz, HCBz, mirex, aldrin and a portion of heptachlor and p,p´-DDE, was eluted with 75 mL n-hexane. The second fraction (F2) that included the rest of the investigated chlorinated pesticides and PAHs was eluted with 70 mL n-hexane/ethyl acetate (1:1 v/v). Each fraction was evaporated with a rotary evaporator. Finally, 1,2,3,4-TCN was added to each fraction (200 pg/µL final concentration) as the internal standard, and the fractions were evaporated under a gentle stream of nitrogen, and brought to a final volume of 1 mL in hexane.

2.7.3. Sulphur removal

In order to remove sulphur that interferes in GC/ECD analysis, copper powder was used according to Sundberg et al. (2005) with some modifications. For each working day, copper powder was washed with concentrated HCl to remove any oxides, and several times with ultrapure water, methanol and acetone. Finally, the powder was dried under a gentle stream of nitrogen. Activated copper powder was added to the obtained fractions and the change of the copper colour from brassy red into black was taken as an indication of sulphur removal. Excess of copper powder was added to ensure that the sulphur was removed completely.

2.8. Determination of organochlorine pesticides and PCBs in mussels

2.8.1. Extraction

About 10 g of each wet homogenized tissue sample was mixed with 70 g anhydrous Na_2SO_4 and 40 g sea sand in a porcelain mortar until a flowing powder was obtained. The mixture was then transferred to a 500 mL conical flask and samples were extracted with 225 mL n-hexane/acetone (2:1) on a horizontal shaker (GFL^R 3020, Progen Scientific, UK) for 20 hours at 220 rpm. Extracts were dried with 10 g Na_2SO_4 and were transferred to a 500 mL rounded flask. Finally, extracts were evaporated on a rotary evaporator and brought to a final volume of 1 mL in hexane using a gentle stream of nitrogen.

2.8.2. Determination of the lipid content

Lipid content was determined according to Qian et al. (1998) with some modifications. A 20 mL aliquot of the tissue extract was removed using a 25 mL graduated cylinder and filtered over a glass fiber filter containing approximately 10 g of anhydrous sodium sulfate that was pre-wetted with n-hexane. The graduated cylinder was rinsed three times with 3 to 5 mL of n-hexane/acetone (2:1 v/v) and the rinses were poured through the filter. A method blank and a duplicate were processed with every sample set. The filtered aliquot was evaporated using the rotary evaporator to near dryness. The residue was quantitatively transferred with n-hexane/acetone (2:1 v/v) to a small vial. The solvent was allowed to evaporate by loosely capping the vial.

A small piece (approximately 1 cm x 2 cm) of glass fiber filter was placed on a corrugated aluminium foil support on a hot plate for a few minutes. The filter was transferred to an electrobalance weighing pan and the balance tarred. The filter was placed back on the hot plate. A 100 µL aliquot of the lipid extract was slowly dotted onto the warm filter. When the solvent had evaporated from the filter, it was weighed again. The relative percent difference (RPD) for the percent lipid values for the original and duplicate sample were calculated.

2.8.3. Clean up with column chromatography

The clean up and fractionation of the tissue extracts followed the method applied for sediments (see 2.7.2.).

2.9. Determination of PAHs in mussels

2.9.1. Extraction

Tissue samples were extracted and cleaned up according to Yunker et al. (1999) with some modifications. About 20 g of each wet homogenized tissue sample was placed in a 250 mL conical flask and 100 mL methanol and 50 % KOH solution (20 mL) were added and the mixture was left at room temperature until complete disaggregation of the mussel tissues. The suspension was transferred to a 250 mL separatory funnel with methanol rinses and extracted three times with 100 mL n-hexane each. The combined extracts were washed three times with 100 mL water and dried over Na_2SO_4 in a glass funnel. The solvent was evaporated in a rotary evaporator and the samples brought to a final volume of 1 mL using gentle stream of nitrogen.

2.9.2. Cleanup with column chromatography

Extracts were cleaned up using a glass chromatographic column (30 cm x 2 cm i.d.) filled with 10 g alumina (deactivated with 12.5 % deionized water) topped with 2 cm Na_2SO_4. After transferring the extract to the top of the column, PAHs were eluted with 70 mL n-hexane. Finally, the eluate was evaporated and brought to a final volume of 1 mL.

2.10. Gas chromatographic analysis

2.10.1. Standards and calibration

For each of the investigated chlorinated compounds (**Table 6**), a single standard stock solution was prepared with a concentration of 1µg/µL. Standard mixtures with a concentration of 10 ng/µL were prepared for the organochlorine pesticides and for the investigated PCB congeners together with the PCBz and HCBz.

Calibration of the chlorinated compounds and the PAHs was performed by external calibration. For the chlorinated compounds, the external standardization was performed at two calibration ranges: 10 to 100 pg/µL and 100 to 5000 pg/µL (The 5000 pg/µl level was only included when the concentration of the analyte was higher than 1000 pg/µL).

For PAHs, the calibration was carried out at a calibration range of 50 to 1000 pg/µL for sediments and 10 to 1000 pg/µL for the mussel samples. When it was necessary, the samples were diluted 10 times to meet the calibration range. The chromatographic peak areas were fitted by linear regression and the calibration was accepted if the coefficient of determination (R^2) exceeding 0.995.

2.10.2. Analysis of chlorinated compounds (GC/ECD)

A Hewlett-Packard gas chromatograph (5890 Series II GC) equipped with a HP 6890 Series injector, a ^{63}Ni electron capture detector (ECD) and a DB-5 fused silica capillary column (J&W Scientific, USA) was used for the analysis of PCBs, PCBz, HCBz and the organochlorine pesticides. 1,2,3,4-Tetrachloronaphthalene was used as the internal standard. A 1.0 µL aliquot was injected respectively. Helium was used as carrier gas and nitrogen as make up gas, the carrier gas flow rate was 2 mL/min and the total flow 60 mL/min. The temperatures of the injector and the detector were kept constant at 250 ^{0}C and 300 ^{0}C respectively. The Hewlett- Packard Chem Station was used for data analysis and management. The results were confirmed using a DB-1701 (J&W Scientific, USA) fused silica capillary column for the sediment and DB-35 MS (J&W Scientific, USA) for the mussel samples. The carrier gas flow rate was adjusted at 1.6 mL/min, and the total flow was 60 mL/min. The temperatures of the injector and the detector were kept constant at 250 ^{0}C and 330 ^{0}C respectively. GC/ECD instrument operation conditions are presented in **Table 15**.

2.10.3. Analysis of PAHs (GC-MS)

GC-MS determination was performed using a Shimadzu (GC-17A) gas chromatograph equipped with Shimadzu AOC-20i programmable auto injector. The gas chromatograph was coupled to a Shimadzu QP 5050A mass selective detector (MSD) with electron ionization mode (EI ionization). The mass spectrometer was operated in selected ion monitoring mode (SIM). The monitored masses are listed in **Table 16**. The ionization source was supplied with voltage at 70 eV. A 1 µL of aliquot was injected into the injector. A DB-5 MS fused silica capillary column with 30 m length, 0.25 µm film thickness and 0.25 mm inner diameter was used (J&W Scientific, USA). The oven temperature program was 60 ^{o}C (5 min) ramped at 10 ^{o}C/min to 300 ^{o}C, hold for 10 minutes. The transfer line temperature was maintained at 280 ^{o}C and the carrier gas (He) flow rate was 1 mL/min.

Table15: Instrument operating conditions for GC/ECD.

Target compounds	Capillary column	Temperature programs
Sediments		
Organochlorine pesticides, PCBz, HCBz and PCBs	DB-5 (60 m×0.25 µm×0.32 mm i.d.)	60 °C (5 min) to 160 °C (3 min) at 10 °C/min, to 220 °C at 2 °C/min, to 280 °C (15 min) at rate 8 °C/min.
PCBs, PCBz and HCBz	DB-1701 (45 m×1.0 µm×0.32 mm i.d.)	80 °C to 160 °C at 30 °C/min, to 220 °C at 10 °C/min, at 5 °C/min to 280 °C (30 min).
Organochlorine pesticides		80 °C to 220 °C (20 min), at 30 °C/min, to 280 °C (15 min) at a ramping rate of 2 °C/min.
Mussels		
Organochlorine pesticides, PCBz, HCBz and PCBs	DB-5 (60 m×0.25 µm×0.32 mm i.d.)	60 °C (3 min) to 160 °C at 20 °C/min, to 250 °C at 2 °C/min, to 280 °C (10 min) at 10 °C/min.
	DB-35 MS (60 m x 0.25 µm x 0.25 mm i.d.)	60 °C to 165 °C at 30 °C/min, to 250 °C at 2 °C/min, to 300 °C (15 min) at 7 °C/min.

Table 16: Masses of PAHs in GC-MS used for SIM.

PAHs	m/z
Nap	128
Acy	152
Ace	154
Flr	166
Phn	178
Ant	178
Fla	202
Pyr	202
BaA	228
Chy	228
BbF	252
BkF	252
BaP	252
InP	276
DibA	278
BghiP	276

2.11. Quality assurance

2.11.1. Determination of the recovery rates

Fortification experiments were performed for all target organic compounds in order to control the extraction and clean up procedures as well as the GC analysis. The percent for each analyte was determined by comparing the determined concentrations with the spiked concentrations. Results were accepted when the recovery rates were in the range of 70 % to 110 % and the RSD % was ≤ 20 %. For sediments, 10 g dw from the reference site (station 5) were spiked with pesticides, PCBs and PAHs at two different levels:

1. 2 µg/kg dw for PCBs, PCBz, HCBz and pesticides and 10 µg/kg dw for PAHs.
2. 25 µg/kg dw for PCBs, PCBz, HCBz and pesticides and 50 µg/kg dw for PAHs

Each spiking concentration was measured 4 times. Obtained recovery rates are summarized in **Appendix I, Tables A2, A3 and A4**.

For the mussels, 10 g ww of mussel tissues (*Mytilus edulis*) bought from a German supermarket were spiked at two different levels as in sediments:

1- 5.5 µg/kg ww for PCBs, pesticides, PCBz and HCBz and 25 µg/kg ww for PAHs.
2- 55 µg/kg ww for PCBs, pesticides, PCBz and HCBz and 100 µg/kg ww for PAHs.

A summary of the obtained results is shown in **Appendix I, Tables A5, A6 and A7** respectively. All recoveries and RSD were within the required ranges except for heptachlor (114 %) in the sediment fortification experiment at the 2 µg/kg dw level. This may be to the fact that heptachlor was divided in the two fractions during the cleanup procedures. Also Fla (116 %) and Chy (113 %) exceeded the 110 % value in the mussel's fortification experiment at the 25 µg/kg ww level. A matrix effect is assumed to be responsible for that.

2.11.2. Method detection limit (MDL)

Metals

For the metals, 4 different concentration levels (0.005 mg/L, 0.01 mg/L, 0.03 mg/L and 0.05 mg/L) were prepared as a mixture of all elements. Each concentration level was prepared 7 times according to the EPA method (USEPA, 1984). To simulate the matrix effect, high concentrations of Na, K, Ca and Mg (1500 mg/L each) were spiked in the standard solutions. The standard solutions were measured with ICP-OES and for each concentration level, the standard deviation and the mean value were calculated. The lowest concentration level that could be determined with a recovery range of 90 % to 110 % and a RSD % ≤ 10 % was defined as the MDL. These MDLs are listed in **Appendix I, Table A8**.

For the mussel samples, which were measured by the ICP-MS, the MDL was determined by measuring blanks 7 times according to the EPA method (USEPA, 1984). MDLs calculated for trace metals are shown in **Appendix I, Table A8**.

Organic compounds

For the organic compounds, the MDL was determined according to USEPA, (1984) and Wisconsin Department of Natural Resources, (1996). The MDL calculation was matrix based. In case of sediments, the low polluted offshore sample (station 5) was used to represent the matrix (10 g dw) and in the case of biological samples, mussels (*Mytilus edulis*) bought from a German supermarket (10 g ww) were used.

The matrices were extracted and cleaned up using the same procedures as described for the samples, and each of the obtained fractions were brought to 1 mL final volume. For the determination of MDL, the cleaned extracts were mixed with selected concentrations of the standard mixtures in a ratio of 1:1 (v/v).

For pesticides and PCBs, matrix based standard solutions were prepared in the range of 1 pg/µL to 7 pg/µl. Each concentration was measured twice to find the suitable level for the MDL determination. In case of sediment samples, 2 pg/µL was selected for chlorpyrifos, 3 pg/µL for o,p´-DDD, p,p´-DDD, o,p´-DDT, p,p´-DDT, methoxychlor, mirex, PCB 101, PCB 126, and PCB 169, 5 pg/µL for β-endosulfane, PCBz, HCBz, PCB 138 and PCB 180, and 7 pg/µl for the rest of the investigated organochlorine pesticides and PCBs. In case of mussels, 3 pg/µL was selected for all the investigated organochlorine pesticides. For PAHs, 75 pg/µL was selected in the case of sediments and 20 pg/µL in the case of the mussel samples. Each selected concentration level was prepared and measured 7 times, the standard deviation (S) for each of the target compounds was calculated and the MDL was calculated according to the following equation:

$$MDL = t_{(n-1,\ 1-\alpha\ =\ 0.99)} \times (S)$$

MDL: method detection limit.
$t_{(n-1,\ 1-\alpha\ =\ 0.99)}$: students t value appropriate for a 99 % confidence level and the estimation of the standard deviation with n-1 degrees of freedom (t = 3.14, n = 7).
S: standard deviation of the replicate analysis (n = 7)

MDL (µg/kg dw) obtained for PCBs, PAHs and pesticides are shown in **Appendix I**, **Tables A9, A10** and **A11** respectively. Several conditions had to be fulfilled in order to calculate the MDL: Firstly, the recovery % of each analyte should range from 70 % to 110 %. Secondly, the calculated RSD % should be ≤ 20 % and finally, the calculated MDL must be larger than one tenth of the lowest spiking concentration (Wisconsin Department of Natural Resources, 1996).

2.11.3. Analysis of certified reference materials

In order to check for the quality of the methods applied for the analysis of trace metals, certified reference materials (BCR: CRM-320-river sediment, Community Bureau of Reference, Geel, Belgium) and (BCR: ERM-CE278 mussel tissues, Community Bureau of Reference, Geel, Belgium) were analyzed with the developed methods. The method was accepted when the recovery of each element was in the range of 90 % to 110 % (see **Appendix I, Tables A12 and A13**).

2.11.4. Repeatability

The analytical repeatability of the results is expressed as relative standard deviation (RSD). 20 % of the total investigated samples were measured as duplicates and the average RSD % for each of the

target compounds was calculated. The precision expressed as RSD % for trace metals, PAHs, PCBs and pesticides in sediments and mussels are shown in **Appendix I, Tables A14, A15 and A16** respectively.

2.12. Statistical analysis

The statistical analysis was performed by SPSS version 13. Statistical analysis included the regression models between the different investigated variables, correlation matrices and testing the significance of a relation between different variables.

3. Results and discussion

3.1. Physicochemical characterization of Abu Qir Bay sediments.

The distribution of grain size in the surfacial sediments revealed the dominance of the sand fraction with amounts above 60 % and often even above 90 % in most of the samples of Abu Qir Bay (**Appendix I, Table A18** and **Figure 8a**). Silt and clay (% fines) contents above 50 % were only observed in front of the Abu Qir Drain (station 21: 56 %), the Abu Qir Fertilizer Company (Stations 2 and 20: 73 and 92 %), the Electric Power Plant (station 15: 62 %), the Petroleum Company (station 13: 52 %) and in front of Maadeya Outlet (station 4: 89 %), which are regarded as the nearshore stations. Fine particle fractions in the range of 30 % to 40 % were observed in stations 1 (Abu Qir Drain), 8 (Maadeya Outlet) and 3 (Electric power plant). These findings were attributed to the detrital particles loaded in the discharges from Abu Qir Drain and Maadeya Outlet. At the same time, the sand fraction started to dominate seawards. This is due to the settlement of the fine particles near the source of entrance until it dropped to values below 10 % near the open sea. Sediments of the western part of the bay were completely dominated with the sand fraction, which is the nature of coastal sediments in the absence of riverine input and/or landbased effluents. The range of the fine fraction (silt and clay) in the present study coincides with those reported for Abu Qir Bay by Aboul-Naga et al. (2002).

pH of the sediment samples ranged from 6.85 (station 3) to 8.10 (station 24). Most of the sediment samples showed close pH values spanning around 7. The Nearshore stations (stations 1, 2, 3 and 4) showed pH values lower than 7 (6.85-6.99). Stations 19, 20 and 24 showed pH values slightly higher than 8.

$CaCO_3$ % in the bay sediments ranged from 16.1 % (station 17) to 47.9 % (station 23) with an average value of 30.5 %. Based on the obtained values of $CaCO_3$ %, samples can be classified into 4 groups. The first group included stations 3, 4, 17 and 26, and was characterized by $CaCO_3$ values lower than 20 %. The second group included stations 6, 10, 11, 13, 14, 15, 16, 25, 28 and 29 with $CaCO_3$ values ranging from 20 % to 30 %. The third group, which included the larger number of sediment samples (stations 1, 2, 7, 8, 9, 12, 18, 20, 21, 22, 27 and 30) and was characterized by values of $CaCO_3$ ranging from 30 % to 40 %. The final group included stations 5, 19, 23 and 24, and was characterized by values of $CaCO_3$ % higher than 40 %.

The total organic carbon (TOC) contents in the bay sediments were generally low (**Appendix I, Table A18**). They ranged from 0.001 % (station 9) to 12 % (Station 21) with an average value of 1.2 %. Values above 1.0 % were only observed in front of Tabia Pumping Station (station 1: 5.8 %; station 21: 12 %), Abu Qir Fertilizer Company (station 2: 6.2 %; station 20: 1.5 %), station 14 (2.4 %), and in front of Maadeya Outlet (station 8: 1.1 %) (**Figure 8b**). These detected higher values are related to the urban and industrial effluents discharged from Abu Qir Drain and the water discharged via Maadeya Outlet. Detected values of TOC were found to decrease in the seaward direction except for offshore

station 14 (2.4 %), which may be related to high biogenic activity as a large amount of shell fragments were observed at this site and/or the circulation pattern of water discharged from the Maadeya Outlet.

Moderate correlation (r = 0.61 at p < 0.01) (**Appendix II, Table A1**) was observed between TOC and clay content in sediments of the bay. The efficiency of fine particles to enrich organic matter by adsorption should be responsible for this finding (Ergin and Yoruk, 1990).

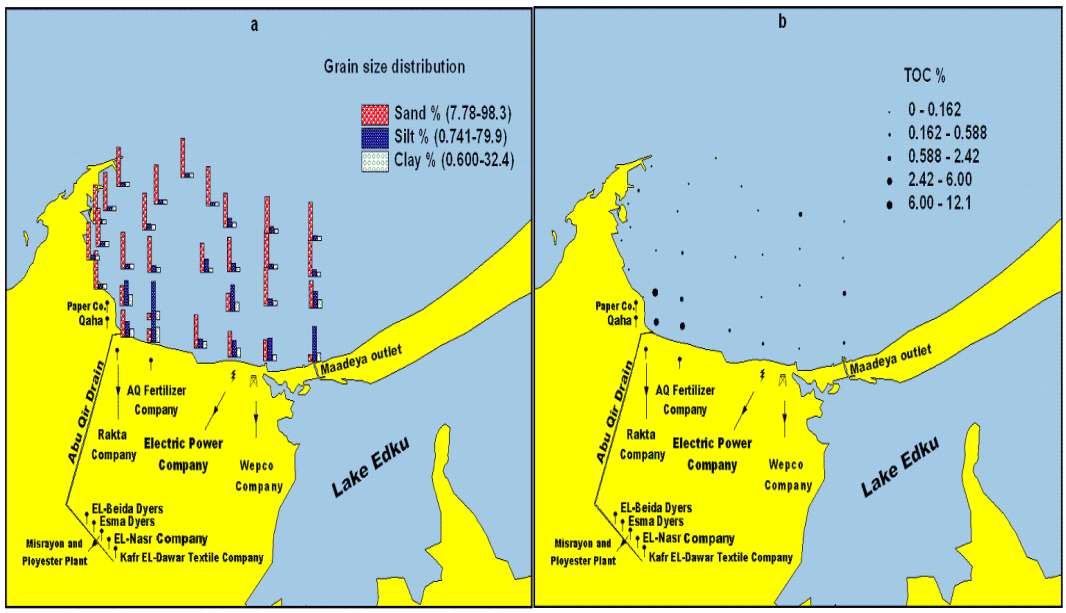


Figure 8: Grain size distribution (a) and TOC (%) (b) in surfacial sediments of Abu Qir Bay.

3.2. Metals in sediments of Abu Qir Bay

Different methods are available for the analysis of trace metals in sediments. Metals can be determined in the whole sediment sample (total digestion method) revealing both the residual and non-residual metals in the different fractions of the sediments (coarse, medium and fine). Another approach initially involves the determination of absolute total metal concentrations in silt and clay (< 63 µm), or other finer fractions separated from the sediments (Banat et al. 1972; Förstner and Salomons, 1980; Loring, 1991). This approach is not normalization in the conventional sense as the absolute concentrations, rather than the total metal concentrations, are determined in relation to a specific size fraction. Although useful for comparative purposes, absolute trace metal concentrations reflect total trace metal levels in only the most general sense. The total trace metal concentration in the sediment depends not only on the absolute concentration in the size fraction, but on the contribution that it makes to the total sample. For example, the < 63 µm fraction might contain 2 mg Cd/kg, but if the fraction constitutes only 10 % by weight of the total sediment, the contribution to the total sediment is only 0.2 mg Cd/kg. Separation of the fine fractions has other disadvantages. Time consuming procedures involving chemical dispersants are required, and they often result in incomplete grain size separation, large volume of samples are required if the sandy texture dominates and

subsequent metal determinations are often inaccurate because of metal loss and contamination (Loring, 1991). For all the above mentioned problems, digestion of the total sediment for total metals determination was selected in the present study. In addition, the SQGs, which were developed for the risk assessment purpose were based on total metal concentrations in the whole sediments, thus to be comparative, the total sediment digestion was selected in this work.

3.2.1. Spatial distribution

Aluminium (Al) and iron (Fe) were determined in the surfacial sediment samples as major elements (**Appendix I, Table A19**). The spatial distribution of the major elements was found to have the same pattern as that of the fine fraction (silt and clay) of the bay sediments, especially the clay fraction (**Figure 9a**). This was confirmed with the high significant positive correlations in the range of 0.70 and 0.91 observed between Al, Fe, clay and the fine fraction in the bay surfacial sediments (**Appendix II, Table 1**). The occurrence of significant correlation between Fe, clay and Al suggests that Fe is partly associated with the clay fraction of the sediments. The same observation was reported by Szefer et al. (1998) in investigating the anthropogenic influx of metallic pollutants into Puck Bay of the south Baltic Sea and Abdelmoeim and Shata, (1993) for Abu Qir Bay sediments. EL-Nozahy and Badr, (1986) showed that sediments of Abu Qir Bay contained some of the Fe minerals such as magnetite, ilmenite, less common hematite and rare limonite.

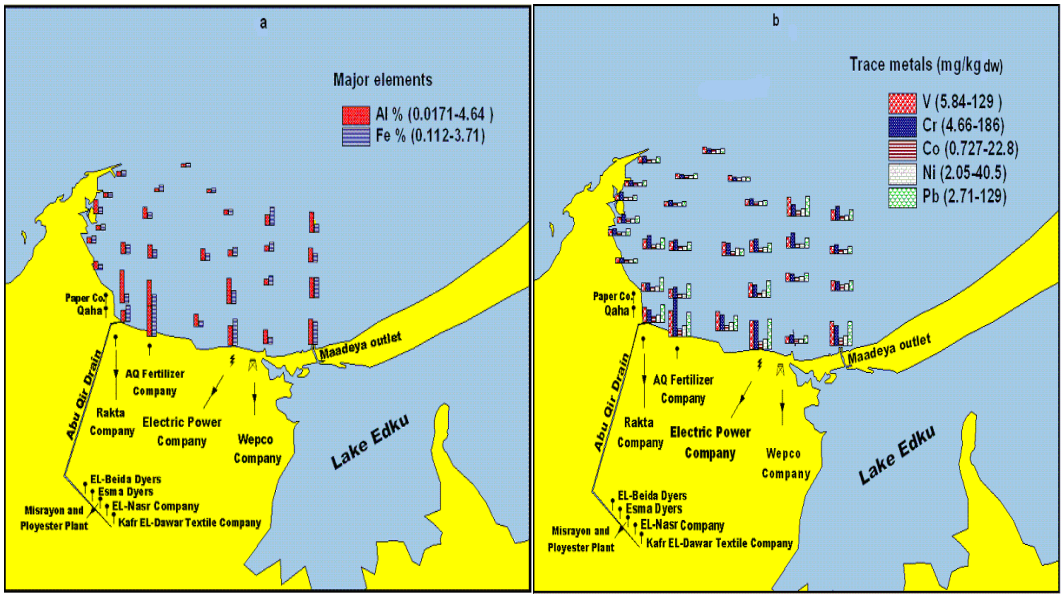


Figure 9: Spatial distribution of trace metals in surfacial sediments of Abu Qir Bay.

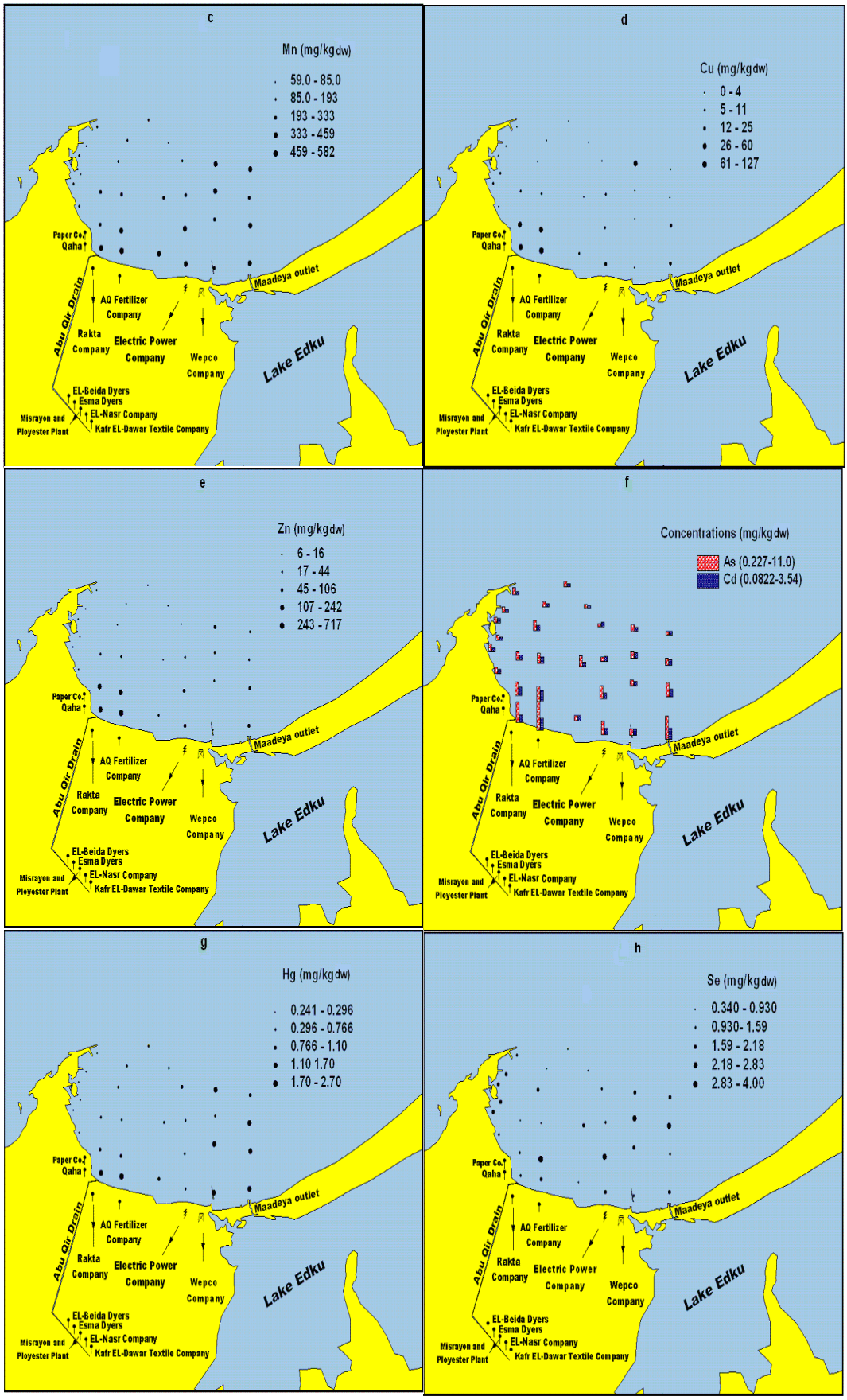


Figure 9: Continued.

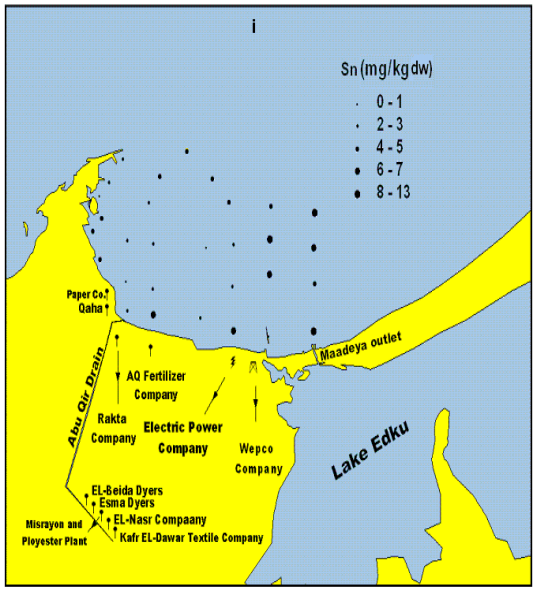


Figure 9: Continued.

Results of the trace metals analysis are summarized in **Appendix I, Table A19**. Higher concentrations of most of the trace metals were found in the nearshore stations in front of the major pollution sources such as the Abu Qir Drain (stations 1 and 21), the Fertilizer Company (stations 2 and 20), the Electric Power Plant (station 3) and the Maadeya Outlet (Station 4), whereas lower concentrations were found in the offshore stations, in the northern (stations 5, to 7) and western parts (stations 25 to 30) of the bay (**Figure 9b-i**). An exception was station 14 in the offshore direction in front of Wepco Petroleum Company, where relatively high concentrations of trace metals were observed compared to the other offshore stations, which may be attributed to the circulation pattern of water in the bay, where the water discharged from the Maadeya outlet moves in the northern and the northwestern direction during the spring, summer and autumn. The concentrations of Cu and Zn in front of Abu Qir Drain (stations 1 and 21) and the Fertilizer Company (stations 2 and 20) were much higher than concentrations recorded in the rest of the bay (**Figure 9d, e**), especially for Zn (**Appendix I, Table A19**).

Hg concentrations in Abu Qir Bay sediments ranged from 0.431 mg/kg (station 6) to 2.70 mg/kg (station 2) with an average concentration of 0.867 mg/kg (**Appendix I, Table A19**). The highest Hg concentrations were found in front of the Maadeya Outlet, the Petroleum Company and the Abu Qir Drain region (**Figure 9g**), whereas lower concentrations were recorded in the northern and the western parts of the bay. The high detected Hg concentrations extend in the seaward direction in the nearshore-offshore profile sampled in front of the Maadeya Outlet and Wepco Petroleum Company.

The spatial distribution of Se in the bay sediments was found to be different as for the other trace metals. Focal points of Se concentrations spread almost all over the bay (**Figure 9h**). Se concentrations in the bay surfacial sediments ranged from 0.342 mg/kg (station 5) near the open sea to 4.00 mg/kg (station 20) in front of the Fertilizer Company with an average concentration of 1.68

mg/kg. Relatively high Se concentrations were recorded in front of the Maadeya Outlet (station 4: 2.01 mg/kg; station 9: 2.83 mg/kg), in the offshore stations in front of the Petroleum Company (station 14: 2.17 mg/kg; station 11: 2.56 mg/kg), in front of the Electric Power Plant (station 3: 2.02 mg/kg; station 15: 2.46 mg/kg) and in front of the Fertilizer Company (station 20).

Sn showed the highest concentration in front of Maadeya Outlet (12.6 mg/kg), whereas the lowest concentration was found in station 21 in front of the Abu Qir Drain (1.32 mg/kg). Higher Sn concentrations were recorded along the nearshore-offshore profile in front of Maadeya Outlet, in station 11 (11.1 mg/kg), station 3 (7.3 mg/kg), station 2 (6.50 mg/kg) and in the offshore stations (**Figure 9i**).

A similar pattern of distribution was recognized for the distribution of the fine grained clay fraction, Al and Fe when compared to the trace metals (except Se and Sn). Significant positive correlations were found between most of the trace metals and Al, Fe and the clay fraction of the sediments and only moderate correlation in the case of Mn (**Appendix II, Table A1**) suggesting that a great portion of the trace metals were associated with the aluminium enriched clay minerals (Summers et al. 1996). At the same time the occurrence of significant correlation with Fe suggests that the trace elements were scavenged by Fe oxyhydroxides during its precipitation due to its high adsorption capacity and affinity for other heavy metals (Moore and Ramamoorthy, 1984). Scavenging of Pb and other metals by Fe and Mn oxides has been observed also in other studies (Rosental et al. 1986; Szefer et al. 1995; Hon-Wah Lam et al. 1997; Glasby and Szefer, 1998). Se and Sn showed weak correlation with Al, Fe and the clay fraction (**Appendix II, Table A1**) suggesting that most of the detected concentrations of these two trace metals were of anthropogenic origin. The same pattern was recognized by Mostafa et al. (2004) in his study on the metal pollution in surfacial sediments of the Western Harbour of Alexandria.

The relatively high concentrations of trace elements in front of Abu Qir Drain and the Fertilizer Company can be attributed to the industrial wastewater discharged via Abu Qir Drain including textile manufacturing, dyers (pigment wastes), paper manufacturing and fertilizers manufacturing, which are known to be anthropogenic sources of trace metals in the aquatic environment (Copson, 1956; Dean et al. 1972; Luh et al. 1973; Förstner and Wittman, 1979; USEPA, 1980; Stokinger, 1981; Lu et al. 1982; Hoffman et al. 1984; Nevens et al. 1990; Dragun and Chlasson, 1991; Ujevic et al. 1998; ATSDR, 2004). Agricultural runoff water (especially phosphate fertilizers) discharged with the water of Lake Edku via Maadeya Outlet are responsible for the elevated concentrations in front of the Outlet (Dean et al. 1972; Grossl et al. 1997; Pezzarossa and Petruzzelli, 2001; Popovic et al. 2001; Prosun et al. 2002; ATSDR, 2004; Wang and Mulligan, 2006). Abu-Hilal, (1987) reported high levels of Cu in phosphate fertilizers (19-48 mg/kg). Combustion of fossil fuels and vehicle emissions may be considered as sources of the trace elements (Pb, Ni, V, As, Cd and Se) in the bay sediments (Gilman et al. 1991; Wren et al. 1995; Grossl et al. 1997; Pezzarossa and Petruzzelli, 2001; Popovic et al. 2001; Prosun et al. 2002; Wang and Mulligan, 2006). The relatively high Cr concentration in front of the Electric Power Plant (129 mg/kg) may suggest that water used in the cooling systems inside the

plant is a source of Cr pollution in the bay as Cr (VI) salts are used as corrosion inhibitor in cooling water devices (Dragun and Chlasson, 1991) and/or the presence of a direct wastewater discharge in the area, which could be a reason of the increase concentrations of some of the investigated trace elements (Pb, Cr, Mn, Ni and V) in front of the Power Plant. High Zn concentrations observed in the bay sediments indicate the increase in the industrial activities in and around the area as Zn is known to be a general indicator for urban development (Förstner and Witmann, 1979).

Lower concentrations of all the investigated metals were observed in the western part of the bay. According to Alam EL-Din and Al-Hogaraty, (2001), circulation pattern in the bay is very complicated and it varies greatly depending on the season and on the wastewater discharged from the major sources of pollution. In winter, thr western part is characterized by an anticlockwise circulation pattern in the surface water. In spring, the Mediterranean waters entring the central part of the bay replace the water in the western part, while in the bottom, the circulation is characterized by shoreward flow. In summer, inshore flow takes place in the western part. These circulation patterns observed in the western part possibly diverge the water away from this region and thus causing less accumulation of pollutants.

3.2.2. Chemical partitioning of trace metals in Abu Qir Bay sediments

Metal speciation was performed on sediments of Abu Qir Bay in an attempt to elucidate the most important metal bearing fractions of the bay sediments, and thus give a better idea about the geochemical behaviour of metals, their mobility, bioavailability and hence their toxicity to the aquatic organisms. The metal speciation process was performed on selected sediment samples that showed elevated total metal concentrations. For the other samples, concentrations were not high enough to be easily detected after the speciation procedure. At the same time, only Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn were included in the metal speciation study. Cd was not included because of its relatively low concentrations in the bay sediments. As, se and Hg were also not includedfor the same reason. Besides, sequential extraction schemes used for metal partitioning were found not to be applicable for the fractionation of As and Se (Tack and Verloo, 1995).

Concentrations of trace metals obtained from the sequential extraction scheme are summarized in **Appendix I, Table A20**. From distributions in the five different operationally defined fractions, three groups could be distinguished: The first group includes Ni and Co and is characterized by the dominance of the residual fraction; followed by the reducible (F3) and finally the exchangeable fraction (F1). The contribution of each fraction to the total concentration is shown in **Figure 10**. The residual fraction represented a mean value of, 58.5 % of the total Co (36.6 %-82.1 %) and 54.9 % of the total Ni (6.27 %-89.9 %). The reducible fraction (F3) represented 28.0 % of total Co (<DL-42.5 %) and 32.6 % of total Ni (<DL-55.3 %). The exchangeable fraction (F1) represented a more significant portion in Co (8.64 %) when compared to Ni (5.05 %). The oxidizable (F4) and the carbonate bound (F2) fractions represented only a minor portion of the total metals in this group.

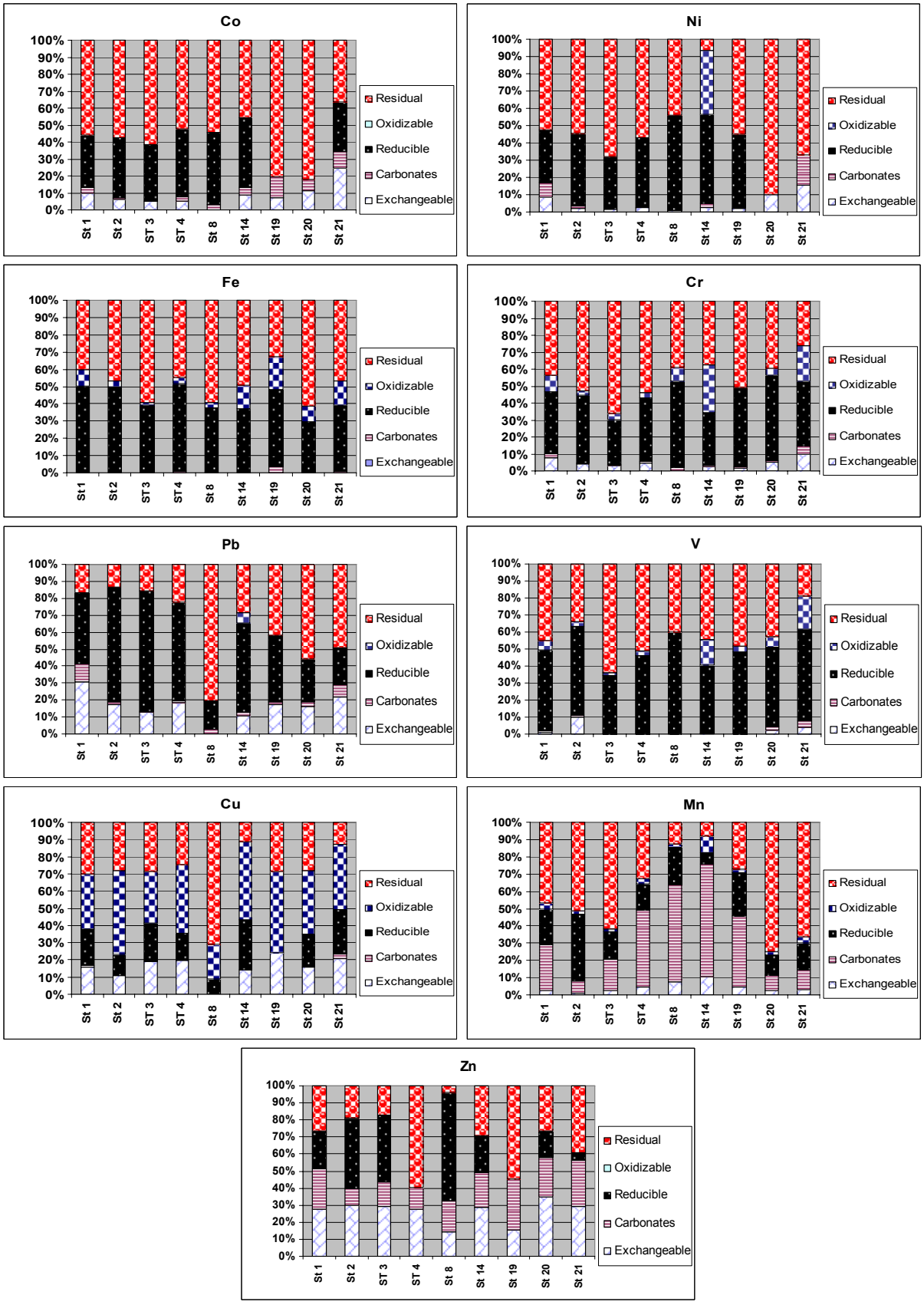


Figure 10: Percent contribution of each metal fraction from the total concentration in surfacial sediments of Abu Qir Bay.

The second group includes Fe and Cr. This group is characterized by the dominance of the residual fraction (F5), followed by the reducible (F3) and finally the oxidizable fraction (F4) (**Figure 10**). The residual fraction represented an average value of 48.3 % of the total Fe ranging from 36.7 % to 61.2 % and 45.4 % of total Cr (26.2 %-66.0 %). The reducible fraction (F3) represented an average of 41.7 % of total Fe (29.5 %-50.3 %), 39.7 % of total Cr (26.5 %-50.8 %). The oxidizable fraction (F4) was generally much smaller than the first two fractions ranging from 0.313 % to 28.4 % in Cr (9.08 %) and from 1.39 % to 21.1 % in Fe (8.77 %).

The third group includes Pb and V, where the reducible fraction (F3) represented the major portion of the total metal concentration ranging from 16.7 % to 71.0 % in Pb with an average value of 43.7 % and from 34.0 % to 59.7 % in V with an average value of 47.5 % (**Figure 10**). The residual fraction (F3) came in the second position with average values of 35.9 % and 43.2 % in Pb and V respectively. The other three investigated fractions had only minor contributions with respect to the total concentrations with the exchangeable fraction (F1) being more significant in the case of Pb (16.1 %) and the oxidizable fraction (F4) in the case of V (6.22 %).

Cu, Mn and Zn had a quite different pattern of distribution between the five investigated fractions (**Figure 10**). Cu was characterized by the dominance of the oxidizable fraction (F4), which represented an average value of 37.6 % of the total Cu concentration (20.1 %-48.7 %), followed by the residual fraction, which represented 29.2 % of the total Cu concentration. The reducible fraction (F3) came in the third position representing 17.2 % of the total concentration (<DL-29.4 %) and finally the exchangeable fraction (F1), which represented 15.5 % of the total concentration (<DL-24.0 %). Cu was not detected in most of the samples in the carbonate bound fraction (F2) (**Figure 10**). Mn was characterized by the dominance of the residual fraction representing 42.4 % (8.27 %-75.0 %) of the total concentration, followed by the carbonate bound fraction (F2), which represented 31.2 % (7.08 %-65.2 %) of the total concentration, then the reducible fraction (F3), which represented 18.9 % (6.52 %-38.6 %) of the total concentration (**Figure 10**).

The exchangeable fraction (F1) and the oxidizable fraction (F4) represented only minor portions from the total concentration. Zn was characterized by the dominance of the residual fraction as most of the investigated trace metals with values ranging from 13.5 % to 77.8 % with an average contribution of 33.6 %. This was followed by the exchangeable fraction (F1), which represented 27.0 % of the total Zn concentration (10.0 %-37.9 %), then the carbonate bound fraction (F2) which represented 21.2 % (7.31 %-42.0 %) of the total concentration and finally the reducible fraction (F3), which represented 19.7 % (0-31.5 %) of the total concentration in sediments of Abu Qir Bay (**Figure 10**).

Based on the average concentrations of the exchangeable fraction (F1), trace metals can be arranged in the following descending order: Zn > Mn > Pb > Cu > Cr > V > Fe > Co > Ni. Assuming bioavailability is related to solubility, then the exchangeable metals are considered the most bioavailable fraction of metals (Tessier et al. 1979). Higher concentrations of the exchangeable metals

(F1) especially Zn, Mn, Cu and Pb were generally observed in the nearshore stations (stations 1, 2, 3, 4, 19, 20, 21) that showed elevated concentrations of total metals at the same time (**Appendix I, Table A19**). It is acceptable that as the metal contamination increase, the easily labile fraction also increase at the same time. The occurrence of these stations near the shoreline makes them vulnerable to the landbased activities thus influencing the behaviour of metals in the sediments. At the same time, relatively high concentrations of exchangeable Co and Mn were also observed in station 14, which is the only offshore station that showed relatively high total concentrations of some of the investigated trace metals. Considering the investigated trace metals, higher concentrations of exchangeable Mn were generally observed in the Maadeya region (stations 4, 8 and 14). On the other hand, Zn, Cu and V showed higher exchangeable concentrations in the Abu Qir Drain region (stations 1, 2, 20, 21), which could possibly indicate the significant role played by the wastewater discharged via Abu Qir Drain in sediment pollution with these trace metals. Co, Cr, Ni and Pb showed higher exchangeable concentrations at Maadeya Outlet and Abu Qir Drain.

The carbonate bound fraction (F2) had a minor contribution in most of the investigated trace metals except for Mn (7.08 %-65.2 %) and Zn (7.3 %-42.0 %) (**Figure 10**). Close results were obtained by Abdallah, (2007) and Van der Veen et al. (2006) in studying the metal speciation in sediments of EL-Mex Bay, West Alexandria, Egypt and the River Elbe respectively. It is well known that the ionic radii of Mn^{2+} and Ca^{2+} ions are similar. Mn^{2+} ions can substitute the Ca^{2+} ion in the crystal lattice of $CaCO_3$ giving up to 4 % (by weight) of $MnCO_3$ (Pingitore, 1978). Menadakis et al. (2007) found that also Zn^{2+} can enter the crystal lattice of calcite. Reducing conditions in the sediments can be deduced from the bounding of manganese with the carbonate fraction (Berner, 1980). A relatively high portion of Mn was extracted in the carbonate bound fraction (F2), which might be explained by the presence of Mn carbonate (Van der Veen et al. 2006). A negligible percentage of Fe was extracted as the exchangeable (F1) and the carbonate bonded fractions (F2) (less than 1 % in all the investigated sediment samples except station 19. This was also reported by Tüzen, (2003).

The reducible fraction represented an important part of the total metals detected in sediments of Abu Qir Bay being in the second order after the residual fraction (**Appendix I, Table A20**). Depending on the obtained percent contribution of this fraction from the total metal concentrations, trace metals can be arranged in the following descending order: V > Pb > Fe > Cr > Ni > Cu > Co > Zn > Mn. A significant portion of Fe was found in this fraction (29.5 %-50.3 % with an average value of 41.7 %) (**Figure 10**). Thus it can be postulated that a significant portion of the Fe located in sediments of Abu Qir Bay is in the form of amorphous hydrous oxides, which are regarded as important metal scavengers especially in the estuarine systems. The occurrence of high portions of the investigated trace metals except for Mn, Cu and Zn in this fraction suggests that Fe oxyhydroxides played an important role in the distribution of trace metals in the bay sediments. Although operationally defined, the reducible phase is believed to consist of hydrous oxides of Fe^{III} and Mn^{IV} (Tessier et al. 1979,; Kersten and Förstner, 1989). These hydroxides are major trace metal hosts in estuarine sediments (Calmano and Förstner, 1983; Jones and Turki, 1997), and have been previously identified as

important bioavailable metal sources (Luoma and Davis, 1983). During early diagenesis, microbially mediated redox reactions quickly result in the reduction of some of these insoluble Fe^{III} and Mn^{IV} oxides, and the release of soluble Fe^{II} and Mn^{II} species to the pore water (Canfield, 1989). Dissolution will also release metals associated with the oxide phases to the pore water, possibly to the overlying water column (Petersen et al. 1995), and to benthic biota.

Except for Cu, the oxidizable fraction (F4), which consists of organic and sulphide bound metals (Tessier et al. 1979; Kersten and Förstner, 1989), showed only minor contributions of all the investigated trace metals as shown in **Figure 10**. Only Cu showed a great association with the oxidizable fraction. Chemical discrimination between the organic and the sulfide phases is difficult (Kersten and Förstner, 1989), but the affinity of Cu for organic particles and coatings is well known (Salomons and Förstner, 1984; Comber and Gunn, 1995). Thus, Cu is most likely deposited in the organically bound form at the sediment surface. Cr on the other hand was also extracted in this fraction with an average value of 9.08 % of the total concentration. Cr has also been known for its ability to be associated probably with organic matter (Jones and Turki, 1997). The extraction of a minor portion of Fe in this fraction suggests that a minor part of iron was found in the anoxic form as FeS, which could possibly arise under anoxic conditions. Most of the Cu and some of the Cr may eventually be fixed as pyrite (FeS_2) (Huerta-Diaz and Morse, 1992) and effectively be immobilized as long as the sediments remain reducing. On the other hand, if significant agitation and mixing occurs between the reducing sediments and oxygen rich water, oxidative degradation of organic matter would be enhanced and Cu and Cr could be potentially mobilized.

The residual fraction (obtained from subtracting the upper 4 fractions from the total), composed of detrital silicate minerals, resistant sulfides, and refractory organics (Tessier et al. 1979) is the most important carrier of all elements studied (**Figure 10**). Metals incorporated into silicate mineral lattices probably account for the bulk of the metals in this fraction, and concentrations should be largely governed by the catchment geology (Carral et al. 1995). According to the average calculated percent contribution of the residual fraction, investigated trace metals can be arranged in the following descending order: Co (58.5 %) > Ni (54.9 %) > Fe (48.3 %) > Cr (45.4 %) > V (43.2 %) > Mn (42.4 %) > Pb (35.9 %) > Zn (33.6 %) > Cu (29.2 %). At the same time, the non-residual (labile) fraction, which is the sum of the first 4 fractions increases in the same order of arrangement. Cu showed the highest mobility, where more than 70 % of the total Cu was found in the non-residual form, thus the majority of Cu can be found in a bioavailable form. As for Pb and Zn, more than 60 % of both trace metals were in the non-residual form. More than 50 % of the total detected concentrations of Fe, Cr, V and Mn were in the non-residual form. Thus it can be concluded that the majority of Cu, Zn and Pb and to a lesser extent Fe, Cr, V and Mn are introduced into the bay from the anthropogenic activities. On the contrary, the majority of Co and Ni were found in the residual form, thus naturally driven in the sediments of Abu Qir Bay. Adamo et al. (1996) demonstrated that Ni in contaminated soils often occurs as inclusions within the silicate spheres rather than as separate grains using scanning electron microscopy and energy dispersive X-ray analysis. The Ni inclusions are protected against natural decomposition as

well as reagent alteration, and only the dissolution of silicates would ensure their extraction. Like the present study, the majority of Co was reported to occur in the residual fraction (Jones and Turki, 1997; Li et al. 2000). Average residual concentrations of Co (6.1 mg/kg dw), Cr (30.5 mg/kg dw), Cu (8.9 mg/kg dw), Mn (159 mg/kg dw), Ni (10.3 mg/kg dw), Pb (21.7 mg/kg dw), V (27.4 mg/kg dw) and Zn (40.4 mg/kg dw) were compared to the background concentrations of trace metals in the average shale as given by Bowen, (1979) and Wedepohl, (1968). All the average concentrations of the investigated trace metals were lower than those of the average shale except for Pb, which was slightly higher. (Van der Veen et al. 2006). The possible explanation is the carry over of PbS from oxidizable extraction step to the residual fraction due to the formation of relatively insoluble Pb sulphate from PbS by the treatment with H_2O_2.

Results obtained from this investigation, where most of the metals are associated with the residual and the reducible fractions or the oxidizable and the residual fractions as in the case of Cu agree to a certain extent with metal speciation studies in sediments from polluted rivers such as Rhine and Elbe (Calmano and Förstner, 1983) and with measurements of metal distribution in the suspended sediment of the Mersey and Humber Estuaries (Comber et al. 1995).

3.2.3. Normalization of metal concentrations in Abu Qir Bay sediments

Because the surface area of sediments is grain-size dependent and controls the adsorption of trace metals in the sediment (Mayer and Fink, 1980), the concentrations of some trace metals correlate with the clay fraction of the sediment that provides the greatest surface area for the adsorption of metals (Jickells and Knap, 1984). However, interpretation of metal concentrations in sediments is compounded by the metal's natural concentration in different minerals and by the relationship of metals to sediment grain size characteristics. Normalization of trace metal data to inorganic chemical constituents such as Al, Fe, Sc and Cs, have been widely used to reduce the natural effect of grain size on trace metal distributions, identify predominant carriers, and to estimate the extent of contamination (Hirst, 1962a, b; Bruland et al. 1974; Ackermann, 1980, Rule, 1986; Windom et al .1989). Al and Fe were both measured in the present study. As shown in **Appendix II, Table A1**, Fe showed higher degree of correlation with most of the investigated trace metals when compared to Al. To examine whether Fe is a conservative element in sediments of Abu Qir Bay, relations between the reducible Fe fraction (F3) and the sum of the first three fractions of each trace metal were drawn as shown in **Figure 11**. At the same time, relations between the residual fraction of Fe and the residual fraction of each of the investigated trace metals are also given in **Figure 11**. From the regression curves, one can observe the strong relationship between the reducible fraction of Fe and Co, Cr, Ni, Pb and V. There was also a relation observed between the reducible Fe and Zn but the strength of the relationship was lower than the previously mentioned trace metals (based on the value of r^2). On the other hand, the residual Fe showed only strong relationship in the case of Co and to a lesser extent Cr and weak or no correlation with the rest of the investigated trace metals (**Figure 11**). Thus it can be concluded that the reactive Fe, which is probably anthropogenically driven is responsible for the high

significant correlation which occurred between total concentrations of most of the investigated trace metals and total Fe.

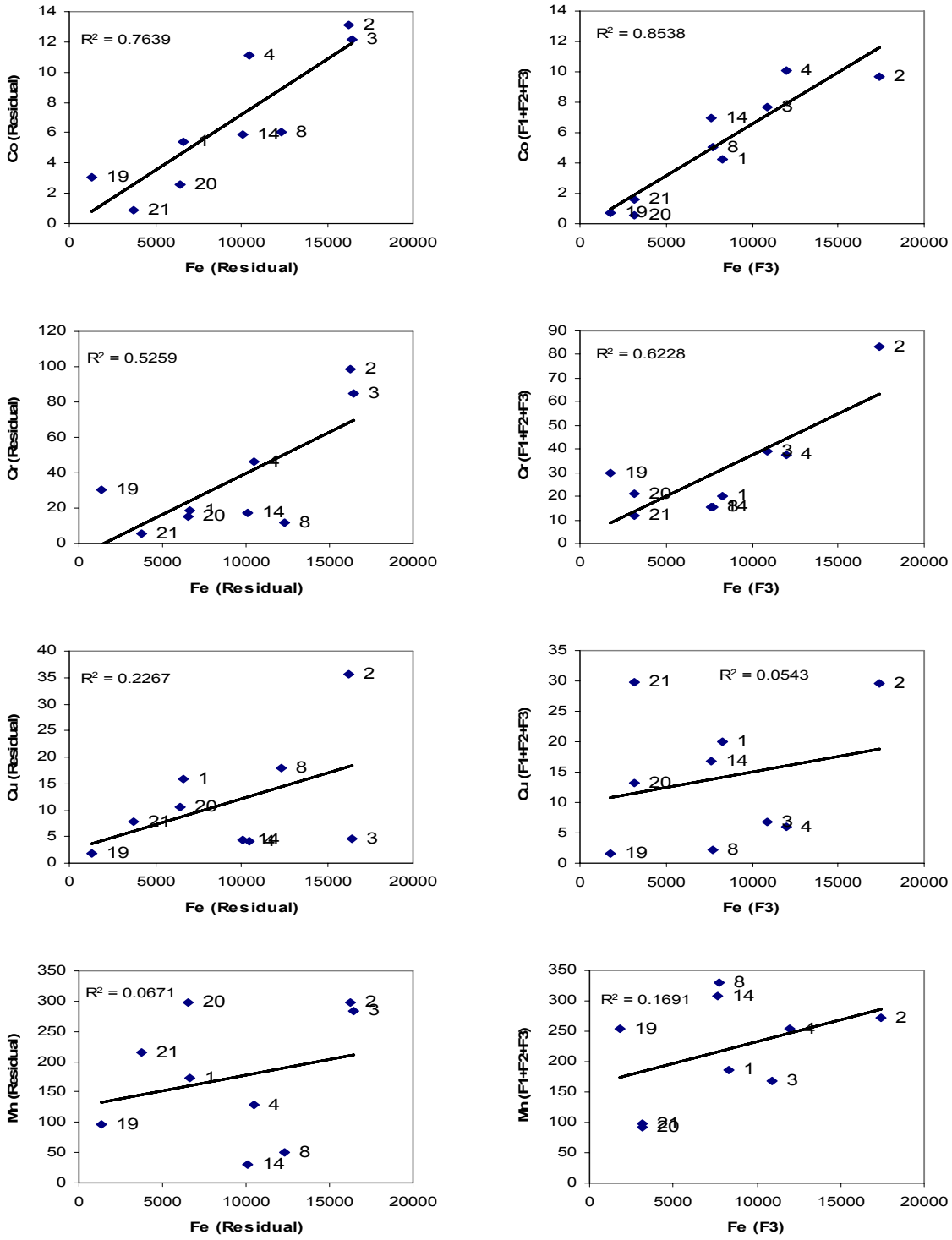


Figure 11: Relations between the reducible fraction of iron (F3) (mg/kg dw) and the sum of the first three fractions (mg/kg dw) of each trace metal and between the residual Fe (F5) and the residual fraction of each of the investigated trace metals.

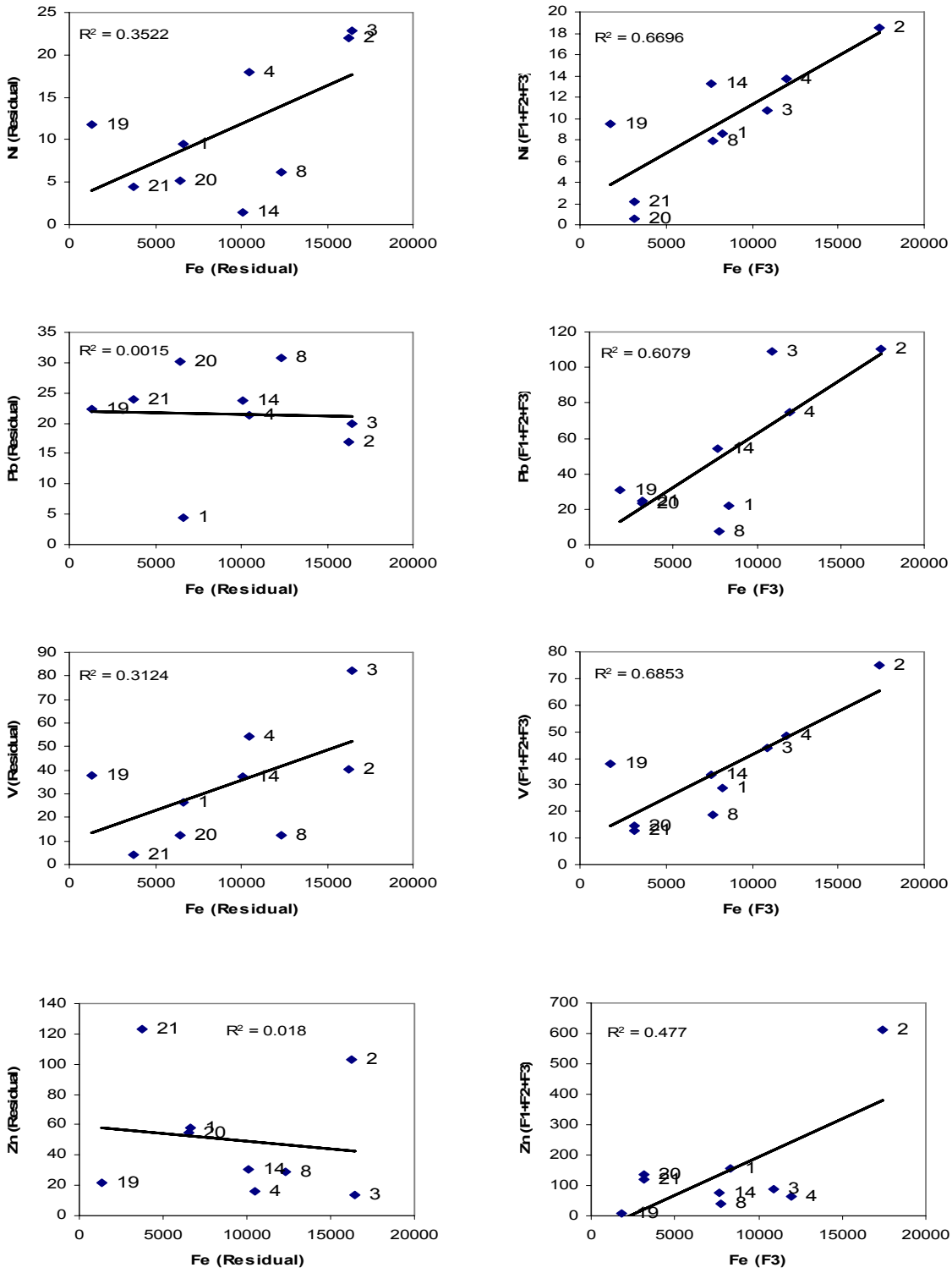


Figure 11: Continued.

Assuming that normalization depends on the use of a conservative element and that conservative means that most of the applied element is located in the crystalline structure of the sediments, which was not the case in Fe, we can conclude that Fe would not be an appropriate choice for the normalization step and that Al should be used instead.

A simple method to distinguish natural changes from those induced by anthropogenic activities is to apply an enrichment factor according to the following formula (Szefer et al. 1998):

$$EF = \frac{\left[\frac{M_s}{Al_s}\right]}{\left[\frac{M_b}{Al_b}\right]}$$

Where,

EF = enrichment factor

M_s = concentration of metal in sediment sample

Al_s = Al concentrations in sediment sample in %

M_b = background concentration of metal

Al_b = background concentration of Al in %

Enrichment factors of one or thereabouts indicates that the element is incorporated in the sediment dominantly as lithogenous material, whereas EFs much greater than one indicates that the element results from anthropogenic sources (Glasby and Szefer, 1998).

The background values used in this study are those of the average shale (Lantzy and Mackenzie, 1979; EL-Sokkary and Muller, 1990) according to Bowen, (1979) and Wedepohl, (1968) due to the fact that it is more representative of the continental soil compared to other geologic materials. Calculated values of the enrichment factors for the surfacial sediments are shown in **Appendix I, Table A21**.

Calculated values revealed that the surfacial sediments of Abu Qir Bay were highly enriched in Se (highest values of enrichment factor ranging from 41.8 to 1556), Cd, Hg and Pb. All the other trace elements showed lower values of enrichment factor (compared with the previous 4 trace elements) except in the case of Sn, where high values of enrichment factors were observed in the offshore stations (stations 10, 11 and 12) in front of the Maadeya Outlet and the Wepco Petroleum Company where high traffic activity occurs and in the western part of the bay (harbour area). Based on the calculated enrichment factors, metals can be arranged descendingly in the following order: Se> Hg> Cd> Pb> Sn > Cr > Zn > Mn > V > Cu > As, Co > Ni > Fe. The influence of anthropogenic activities was obviously expressed in stations 1, 2, 3,10, 11, 12, 14, 16, where most of the investigated trace elements showed values of enrichment factors higher than 1 (**Appendix I, Table A21**). The influence of anthropogenic activities can also be observed in stations 4, 8, 9, 17, 18, 19, 22, 23, 27, 28, 29 and

30 but to a lesser degree when compared to the previous stations. These findings were in agreement with results obtained from the sequential analysis, where most of the investigated nearshore stations showed higher proportions of the non-residual metal fraction. At the same time, trace metals like Pb, Cr, Zn and Cu, which showed higher ability of mobility in the bay sediments, were also characterized by elevated enrichment factors values and in the majority of the investigated samples. It can be then concluded that although the nearshore sediments were enriched in trace metals, sediments that were away from the direct wastewater inputs but could be influenced by the circulation pattern in the bay were greatly enriched by trace metals and thus the influence of the anthropogenic activities in enriching sediments with trace metals can be easily observed in the whole bay.

The enrichment factors in the western part of the bay indicate enrichment with most of the investigated trace metals. High values were found especially for Sn, Se, Pb, Cu and Cr, elements that are supposed to result from shipping activities (repairment, painting and traffic motion) that are greatly concentrated in this region. At the same time, domestic wastes discharged from this urbanized area, might have caused metal enrichment in the sediments of this area.

Higher Sn concentrations compared to the other locations along the nearshore-offshore profile in front of the Maadeya Outlet are attributed to the intensive shipping activities of fishermen coming from Lake Edku and crossing the Maadeya Outlet to the bay.

3.2.4. Comparison of sediment trace metal concentrations with concentrations worldwide

Concentrations of the investigated trace elements were compared with concentrations reported in other studies as shown in **Appendix I, Table A22**. Compared to other locations worldwide, sediments in the present study had higher concentrations of some and lower concentrations for other trace metals when compared to concentrations reported (**Appendix I, Table A22**). Selected examples of previous studies performed in sediments worldwide are shown in **Figure 12**. Great variability was observed in the detected concentrations of trace metals in the bay sediments when the different studies were compared with each other. For example, the concentrations of most trace metals (Pb, Cd, Cu, Ni and Cr) reported by EL-Sokkary, (1993) according to the samples collected in 1985 were much higher than concentrations recorded in the present study and all the other studies on Abu Qir Bay. On the contrary, Cd concentrations reported by Aboul-Naga et al. (2002) were lower than those reported in the present study and the study performed by Saad et al. (1980) (**Appendix I, Table A22**). Zn concentrations determined in the present study were within the same range as those determined by Saad et al. (1980). Sn concentrations determined in the present study were higher than those determined by Abdel-Fatah, (2006) (**Appendix I, Table A22**). Cr concentrations determined in the present study were much lower than those reported by Aboul Dahab, (1989) and EL-Sokkary, (1993), which may indicate that there was a great decrease in the amount of Cr discharged into the bay. As shown in **Figure 12**, higher concentrations of As, Cr, Cu, Pb, Sn and Zn are generally observed in the Western Harbour of Alexandria, Egypt. Cd showed relatively higher concentrations compared to Aegean Sea, the Western Harbour, Egypt and concentrations recorded in the bay sediments in 2002.

On the other hand, Cd concentrations were much lower than concentrations recorded in the bay in 1980. Because little data are available for metal concentrations in the bay sediments, no specific time trend could be observed for the investigated metals when compared to the previous concentrations recorded in the bay sediments. However, detected concentrations in the present study revealed that except for Cr, no marked significant decrease or increase in the metal concentrations could be recognized for surfacial sediment concentrations of Abu Qir Bay. It must be pointed out that the samples from the present study and the previous studies on Abu Qir Bay might be collected from different sites and intervals in addition to different analytical methods, which could contribute to some of the differences in the metal concentrations.

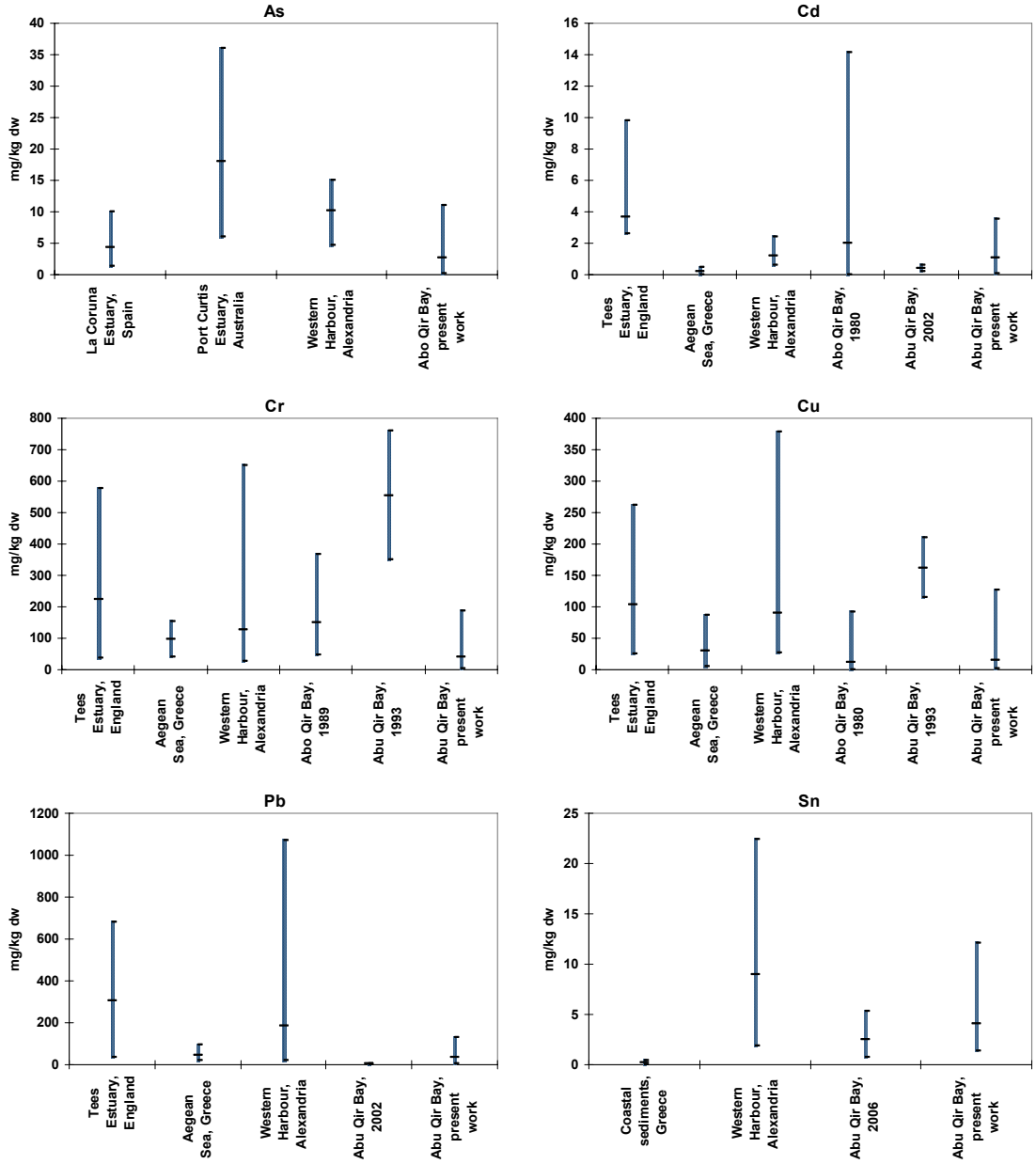


Figure 12: Ranges and average concentrations of metals (mg/kg dw) in some representative surfacial sediments worldwide, along the Egyptian Coast and previously performed on Abu Qir Bay compared to the present work.

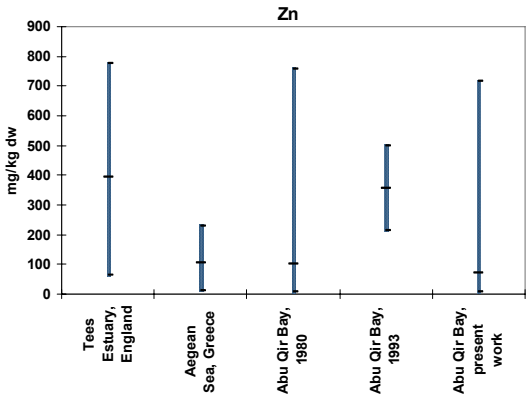


Figure 12: Continued.

3.3. Trace metals in the mussel samples of Abu Qir Bay

3.3.1. Spatial distribution

Several composite samples of bivalves were collected from Abu Qir Bay comprising 7 samples of *Mactra corallina* (in front of the Maadeya Outlet, the Petroleum Company and between the Electric Power Plant and the Fertilizer Company) and 6 samples of *Tapes decussata* (in the western part of the bay). Two species were selected because none of them covered the whole bay. At the same time, both species were present only in 13 out of the 30 investigated sediment samples. In the other locations, either empty shells or completely no samples were found. Selected trace metals (As, Cd, Cr, Cu, Hg, Mn, Pb, Se and Zn) were only analyzed in the mussel samples. The selection was based on the toxicity of the metal both to the mussel itself and to the humans and the availability of guidelines in the risk assessment process.

The concentrations, expressed on a dry weight basis of the trace metals, in the different species are shown in **Appendix I, Table A23** and **Figure 13**. Trace metals concentrations in *Mactra corallina* showed the following descending order: Mn > Zn > Cu > As > Cr > Pb > Se > Hg > Cd. High concentrations of trace metals were generally observed in samples located in front of Maadeya Outlet and the Petroleum Company owing to the polluted water discharged from the Maadeya Outlet. No great variations were observed for the concentrations of trace metals between the different locations (**Figure 13**) except for Cr, Zn and Mn, where concentrations of Mn recorded in front of Maadeya Outlet and the Petroleum Company were 20 times or more higher than those recorded in the other stations or even in *Tapes decussata* (**Appendix I, Table A23**). The average concentration of Mn was 105 mg/kg dw. Slightly higher concentrations of Zn were recorded in stations 4 (74.2 mg/kg dw), 8 (71.2 mg/kg dw) and 10 (68.3 mg/kg dw). Concentrations ranged from 42.6 mg/kg dw (station 9) to 74.2 mg/kg dw. Cu ranged from 8.26 mg/kg dw (station 13) to 12.7 mg/kg dw (station 8) with an average concentration of 10.5 mg/kg dw. As ranged from 6.25 mg/kg dw (station 18) to 12.1 mg/kg dw (station 4) with an average concentration of 9.36 mg/kg dw. For Cr, variations were observed for the concentrations at the different locations, where concentrations recorded at stations 9 and 19 (1.81 and 1.62 mg/kg dw respectively) were much lower than concentrations recorded at all the other stations.

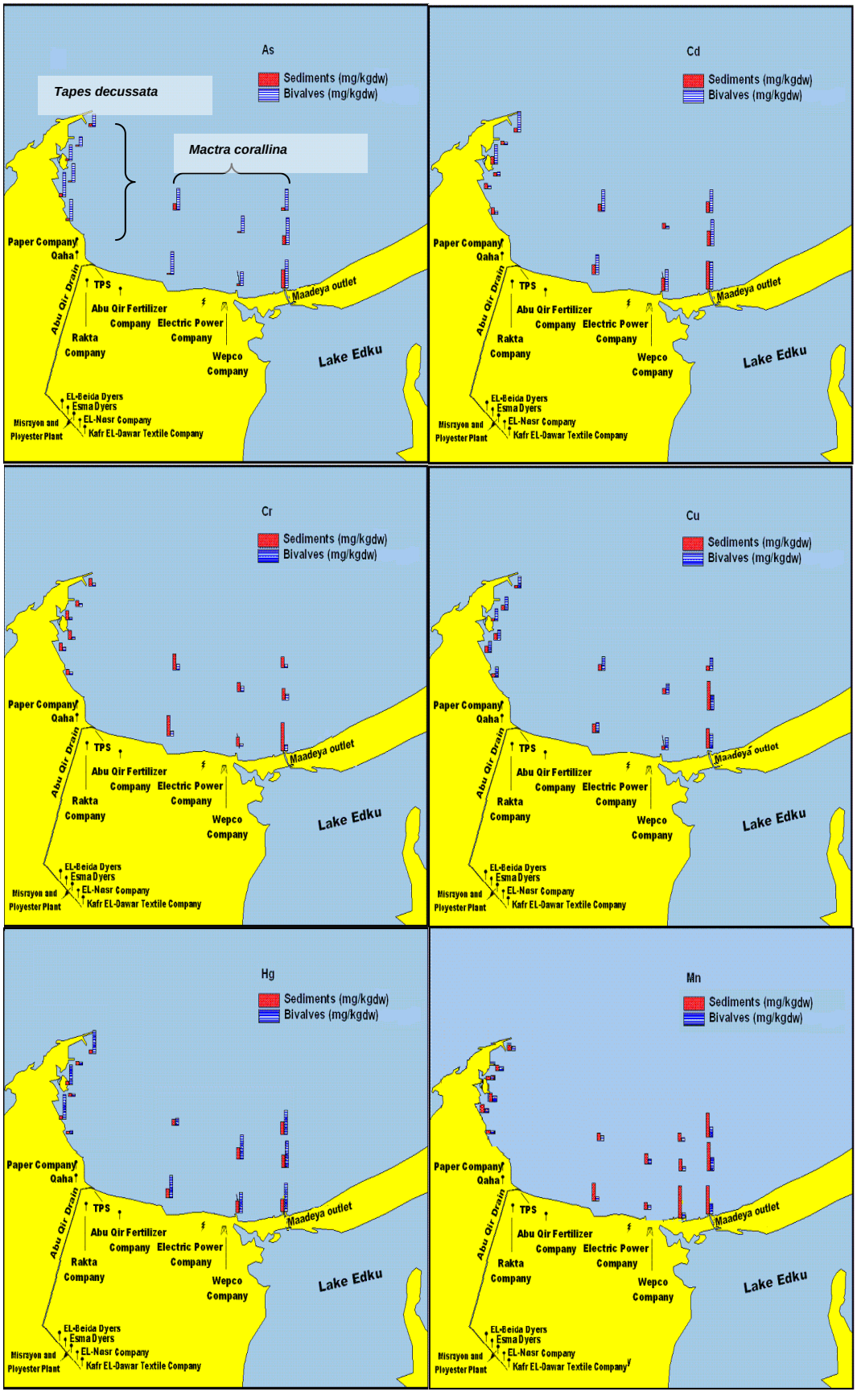


Figure 13: Concentrations (mg/kg dw) of trace metals in mussel samples of Abu Qir Bay compared to the sediment samples.

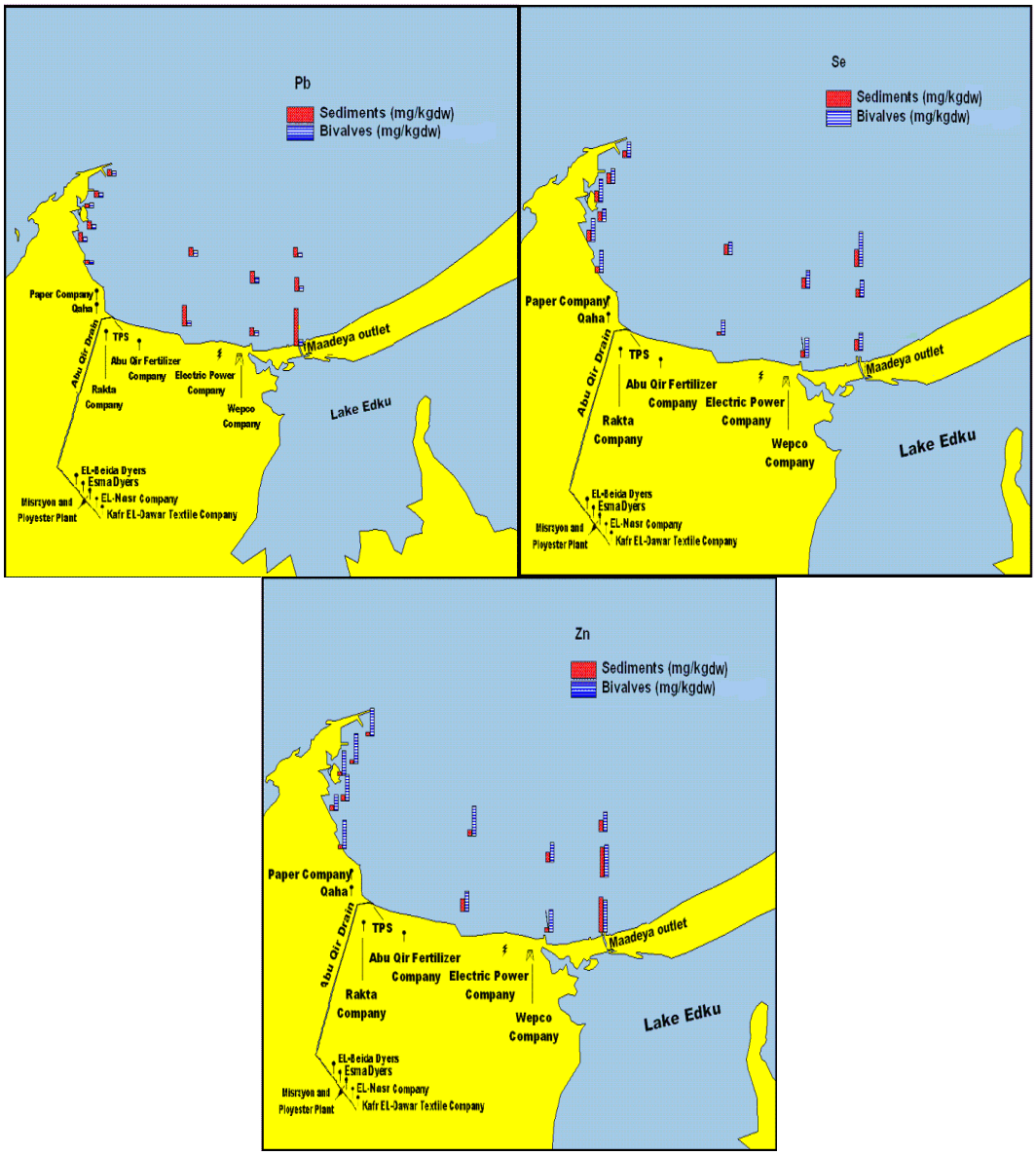


Figure 13: Continued.

Pb concentrations ranged from 5.46 mg/kg dw (station 9) to 10.5 mg/kg dw. Except for station 9 (5.46 mg/kg dw), close Se concentrations in the range of 2-4 mg/kg dw were observed in all the sampled stations (**Appendix I, Table A23**). Hg concentrations ranged from 0.8 mg/kg dw (station 12) to 3.46 mg/kg dw (station 4) with an average concentration of 2.65 mg/kg dw. With the exception of station 12, close concentrations were observed between the different stations. Close Cd concentrations were observed at different stations except for station 18, where the detected Cd concentration was much lower than the rest of the investigated stations.

A different descending order for trace metals was observed in *Tapes decussata* (**Appendix I, Table A23**): Zn > Cu > Mn > As > Pb > Se > Cr > Hg > Cd. The average concentrations of trace metals in *Tapes decussata* were generally lower than those in *Mactra corallina*. Opposite to what was observed

in *Mactra corallina*, variations in the concentrations of As, Cd, Cr, Pb and Hg were observed between the different investigated samples.

Concentrations of trace elements recorded in both species were compared using the student's t-test to evaluate whether they exhibit any significant difference or not. Data revealed that there is an insignificant difference between concentrations of As, Cu, Se, Zn and Hg between both species (at 5% level of significance). On the contrary, concentrations of Cd, Cr, Mn and Pb are significantly higher in *Mactra corallina* than in *Tapes decussata*, which can be related to the location of *Mactra corallina* being affected by wastewater discharges from the Maadeya Outlet and the Abu Qir Drain. It must be pointed out that the physiological differences between the species and/or differences in the exposure of the organisms due to physico-chemical conditions and metal distribution between dissolved and particulate phases and the difference in the bioaccumulative capacity of different trace metals in different species may have resulted in this different pattern of metal distribution.

3.3.2. Relation between trace metals in mussel tissues and sediment samples

Concentrations of trace metals recorded in the mussel tissues were compared to their corresponding sediment concentrations to evaluate any possible relation (**Figure 13**). Tissues of both species contained relatively high concentrations of most metals at most sites compared with sediments. Higher As concentrations were observed in tissues of *Mactra corallina* in front of the Maadeya Outlet and to a lesser extent between the Electric Power Station and the Fertilizer Company (stations 18 and 19), where higher As concentrations in sediments were recorded (**Figure 13**). A positive significant correlation was observed between As ($r = 0.80$), Cu ($r = 0.80$), Se ($r = 0.84$) and Zn ($r = 0.80$) concentrations in sediments and tissues, which may indicate that the detected concentrations of these trace elements in tissues of *Mactra corallina* were greatly related to the metal concentrations in the bay sediments (high bioavailability of these trace metals). In the case of Cd ($r = 0.65$), Cr ($r = 0.62$), Mn ($r = 0.7$), and Pb ($r = 0.73$), moderate degree of correlation was recorded. Trace metal concentrations in mussels were compared to bioavailable metal concentrations in the bay sediments (the sum of the first 4 fractions of the sequential extraction procedure). High significant positive correlation was observed in the case of Zn ($r = 0.9$), Pb ($r = 0.9$), Mn ($r = 0.8$) and to a lesser extent Cu ($r = 0.7$). For Zn, Pb and Mn, a significant portion of the total concentration was found in the exchangeable (Pb and Zn) and the carbonate bonded fractions (Mn and Zn), which are regarded as the most bioavailable forms whereas in Cu, the greatest portion of total Cu was found in the oxidizable fraction (bonded to organic matter and/or sulfides), which could explain the lower degree of correlation as this fraction is less biovailable compared to the exchangeable and carbonate bonded fractions.

In contrast to *Mactra corallina*, detected concentrations of trace metals in tissues of *Tapes decussata* showed weak or no correlation with sediment concentrations. This can be explained if we consider that concentrations of trace metals in sediment samples of western part of the bay (where the samples of *Tapes decussata* were taken) are low in sediments, probably lower than a threshold above which these organisms are able to regulate the accumulation of metals in their bodies (Usero et al. 2005).

Mactra corallina when sampled, were buried in the bottom sediments, whereas *Tapes decussata* was obtained from solid substrates and rocks present in the western part of the bay (not in direct contact with sediments), which can be another reason for the absence of correlation between metal concentrations in tissues of the bivalve and their corresponding sediments.

Previous studies on metal concentrations in marine bivalves have shown good correlation (Ruiz and Salinas, 2000; Shulkin et al. 2003; Usero et al. 2005; Negri et al. 2006) as well as weak correlation with the corresponding sediment concentrations (De Mora et al. 2004).

It is generally agreed that heavy metal uptake occurs mainly from water, food and sediment. However, effectiveness of metal uptake from these sources may differ in relation to ecological needs and metabolism of animals and concentrations of the heavy metals in water, food and sediment as well as some other factors such as salinity and temperature (Heath, 1987; Langston, 1990; Roesijadi and Robinson, 1994).

3.3.3. Comparison of mussel trace metals concentrations with concentrations worldwide

Concentrations of trace metals in the mussel tissues were compared with concentrations recorded in other bivalve species in different locations worldwide and in previous studies conducted on Abu Qir Bay (**Appendix I, Table A24**). **Figure 14** shows concentrations of metals recorded in mussel species worldwide and along the Egyptian Coast, in addition to concentrations recorded in the present study in both species. It was found that in the present study, concentrations of As, Hg and Pb were higher in both species compared to concentrations recorded in mussel samples of Spain, Australia, Israel, and concentrations previously recorded in mussel species along the Egyptian Coast. On the other hand, Cu concentration in both species was within the same range as concentrations recorded in Israel (although slightly higher) and previously recorded in Abu Qir Bay. At the same time, Cu concentrations were much lower than concentrations recorded in mussel species and oyster of Spain and Australia respectively. Taking a close look to **Table A24**, one can observe that concentrations of trace metals in the present study were higher than concentrations recorded in different species along the Alexandrian Coast. In the study performed by Mohamed and Khaled, (2007), slightly higher average As and higher Pb concentrations were recorded in the algae *Corallina mediterranea* and higher average Pb concentration was observed in *Ulva lactuca* in Abu Qir Bay. On the other hand, higher concentrations of trace metals were recorded in bivalve tissues of Abu Qir Bay when compared to detected concentrations of trace metals in some fish species sampled from Abu Qir Bay and other parts along the Alexandrian Coast (**Table A24**). As for the bivalves, higher concentrations of most trace metals were observed in this study compared with the previous studies. The only exception was with Cd, where higher concentrations were recorded in *Donax trunculus* (Ghazaly, 1988; Ahdy, 1999). The higher detected concentrations of trace metals in *Mactra corallina* compared to the previous studies could be related to species difference, difference in sampling locations, difference in the sampling periods, and difference in the analytical techniques.

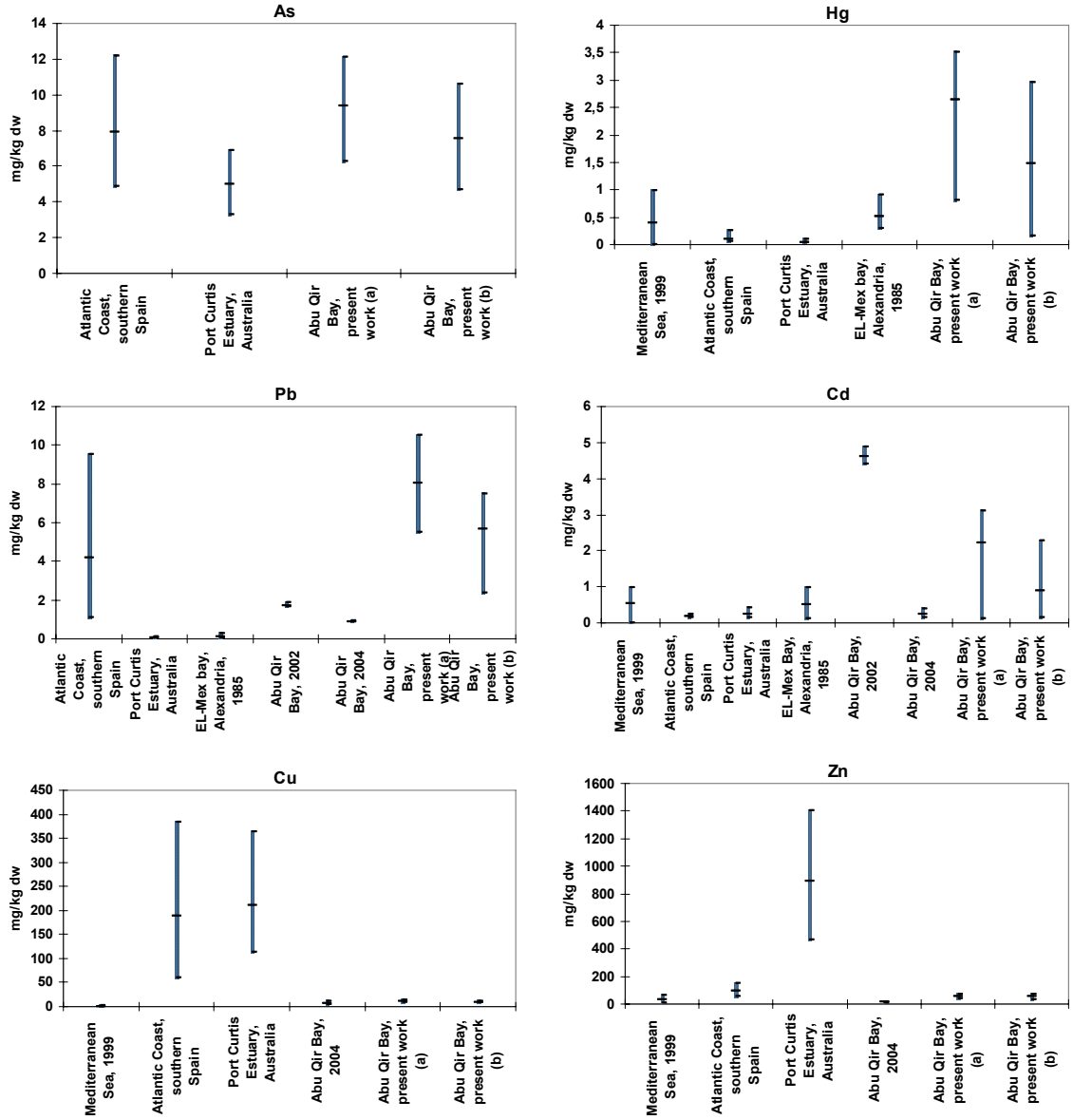


Figure 14: Ranges and average concentrations of metals (mg/kg dw) in mussel species worldwide, along the Egyptian Coast and previously performed on Abu Qir Bay compared to the present work. (*Donax trunculus* in Spain; *Mactra corallina* in the Mediterranean Sea, Israel; oyster in Australia; *Mactra corallina* in EL-Mex Bay and *Donax trunculus* in Abu Qir Bay, 2002 and 2004; a: *Mactra corallina*; b: *Tapes decussata*).

3.4. Polychlorinated biphenyls (PCBs) in the sediment samples of Abu Qir Bay

3.4.1. Spatial distribution and possible sources

Trace organic pollutants were analyzed in only 20 sediment samples from Abu Qir Bay. The selection strategy depended on starting with the nearshore stations, and then going seaward using the same sample locations used for trace metals analysis until the concentrations were below or just above the detection limit. In the present study, PAHs, PCBs, organochlorine pesticides, chloropyrifos, PCBz and HCBz were analyzed in the bay sediments. These pollutants were selected because some were previously detected in sediments of Abu Qir Bay and because of their ecotoxicological hazard.

The PCB congeners determined and reported here were the 6 congeners being selected in several countries to determine whether PCB levels in food products, waste mineral oil and environmental samples comply with the maximum levels permitted by legislations (Anon, 1984, 1988; Wells et al. 1988; De Boer and Dao, 1991). These congeners given in sequence of elution in the chromatograms are PCB 28 (2, 4, 4' –tri CB), PCB 52 (2, 2', 5, 5' –tetra CB), PCB 101 (2, 2', 4, 5, 5' –penta CB), PCB 153 (2, 2', 4, 4', 5, 5' –hexa CB), PCB 138 (2, 2', 3, 4, 4', 5' –hexa CB) and PCB 180 (2, 2', 3, 4, 4', 5, 5' –hepta CB). This approach in the legislation instead of the total PCB content was applied in Germany according to Deutsches Institut für Normung, DIN 51 527, part 1, (1987) and in the Netherlands (Wegener et al. 1988). The selected 6 congeners represent different levels of overall chlorination of the molecule and also differ in the site of the chlorine atom substitution to the biphenyl skeleton. The numbering of the congeners is shown according to the IUPAC rules as suggested by Ballschmiter and Zell, (1980). Apart from these, a number of other congeners such as PCB 70 (2, 3', 4', 5 –tetra CB), PCB 118 (2, 3', 4, 4', 5 –penta CB), which are widely detected in environmental samples and the coplanar PCBs; PCB 126 (3, 3', 4, 4', 5 –penta CB), PCB 156 (2, 3, 3', 4, 4', 5 –hexa CB) and PCB 169 (3, 3', 4, 4', 5, 5' –hexa CB), which are known as dioxin like PCBs and belong to the 12 most toxic PCB congeners (Fernandez et al. 1999).

PCB concentrations given as the sum of the 11 investigated PCB congeners are shown in **Figure 15** (concentrations of each congener are shown in **Appendix I, Table A25**). Concentrations ranged from <DL to 22.2 µg/kg dw with an average concentration of 5.68 µg/kg dw. The highest concentrations of PCBs were observed in front of Abu Qir Drain (station 1: 20.6 µg/kg dw and station 21: 9.71 µg/kg dw), in front of the Fertilizer Company (station 2: 22.5 µg/kg dw and station 20: 13.1 µg/kg dw), between the Fertilizer Company and the Electric Power Plant in the nearshore direction (station 19: 7.25 µg/kg dw), in front of the Maadeya Outlet (station 4: 15.0 µg/kg dw, station 8: 6.01 µg/kg dw) and station 14 in front of the Wepco Petroleum Company in the offshore direction (9.21 µg/kg dw. PCBs were completely not detected in the reference site (station 5), the western part of the bay (stations 25, 26, 27) due to the circulation pattern and at stations 12 and 23. The geographical distribution of PCB contamination revealed that PCB contamination spread in Abu Qir Bay except for the western part. No published data are available for the amount of input of PCBs into the bay and whether any point sources exist (Barakat et al. 2002), but the past use of these substances in transformers, electrical equipments, ship paints and other industries have been common and could possibly be the main

source of PCBs in the bay. The spatial distribution of PCB concentrations in sediments of Abu Qir Bay suggests that the industrial and agricultural waste water discharges via Abu Qir Drain and the Maadeya Outlet are possibly regarded as major sources of contamination with PCBs. The presence of the paper and pulp industry in addition to the other industries and shipping activities could greatly contribute to the sediment contamination with PCBs.

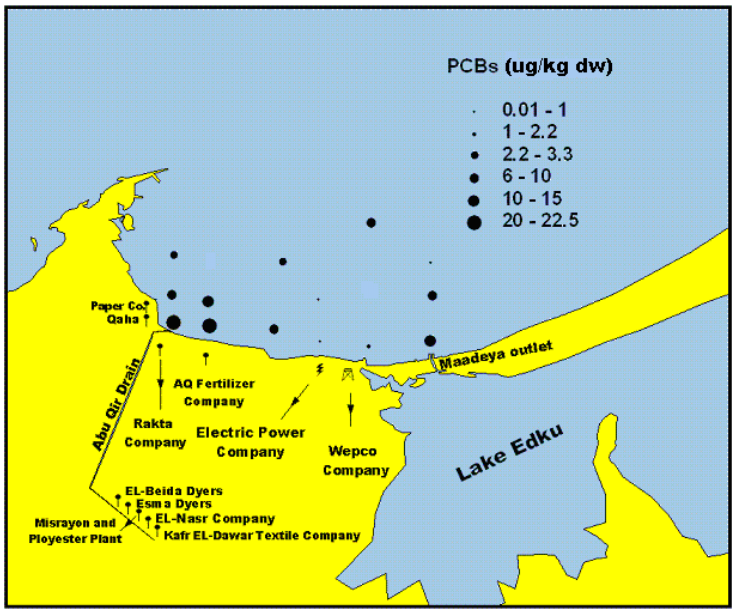


Figure 15: Spatial distribution of PCBs in surfacial sediments of Abu Qir Bay.

Intermediate degree of correlation was observed between concentrations of PCBs in sediments of Abu Qir Bay and TOC % ($r = 0.62$ at $p < 0.05$) and clay % ($r = 0.69$ at $p < 0.05$). Coakly et al. (1993) and Achman et al. (1996) found no correlations between total PCBs and TOC but a difference was noted for the varying types of TOC found suggesting that the origin of the TOC must be taken into account. Studies in the Clyde Estuary, UK (Balls et al. 1997; Hess, 1998; Edgar et al. 1999) could not identify a strong correlation between PCBs and TOC or particle size. In Abu Qir Bay, although higher concentrations of PCBs were observed in sediments characterized by higher TOC % and higher values of the fine fraction, the spatial distribution in the bay sediments could possibly be related to the distance from the major sources of effluents discharged into the bay.

Based on their detection frequency, the selected 11 PCB congeners can be arranged in the following descending order: PCB 153 (70 %) > PCB 180 (65 %) > PCB 138 (60 %) > PCB 70 (55 %) > PCB 101 (50 %) > PCB 118 and PCB 28 (45 %) > PCB 52 (40 %) > PCB 156 (30 %) > PCB 126 (20 %) > PCB 169 (15 %). This order reveals that hexa and hepta chlorinated biphenyls are more frequently detected in the sediment samples of Abu Qir Bay. Based on average concentrations, the most abundant congeners detected in sediment samples were PCB 70, PCB 153, PCB 118, PCB 138 and PCB 101, which are usually found in the environmental samples as shown in literature. In addition, PCB 180,

PCB 52 and PCB 28 were found at intermediate concentrations. The latter PCB congeners have low to medium toxicity. Concentrations of the more toxic PCB congeners such as PCB 126, PCB 156 and PCB 169 (Fernandez et al. 1999) were below the detection limit in most of the investigated sediment samples, but also these toxic PCB congeners were detected in stations with the highest concentrations of all PCBs representing from 7.2 % (station 4) to 24.3 % (station 14) of the total concentrations of all PCBs.

Concentrations of PCBs based on the number of the chlorine atoms are shown in **Figure 16**. As suggested by Hong et al. (2003), high chlorinated PCBs with high K_{ow} values are more likely to be adsorbed to suspended particulate material than lower chlorinated PCBs. These materials then probably settle onto the bottom sediments near the source. Persistence of PCBs in aquatic sediments is due to their low rate of degradation and vaporization, low water solubility, and partitioning to particles and organic carbon (Kennish, 1992). The physicochemical properties as well as the degradation of PCBs vary and depend on the number and position of chlorine atoms in the biphenyl rings (Reutergarth, 1980; Abramowicz et al .1993; Rhee et al. 1993). PCB congeners in sediments of Abu Qir Bay were dominated by tetra, penta and hexa chlorinated biphenyls. The dominance of higher chlorinated biphenyls over the lower chlorinated ones in sediments of Abu Qir Bay could be related to the higher water solubility of lower chlorinated biphenyls (Edgar et al. 2003). Edgar et al. (1999) reported that the occurrence of tetra, penta, hexa and hepta chlorinated biphenyls in sediments makes the composition similar to that of the industrial mixture Aroclor 1254.

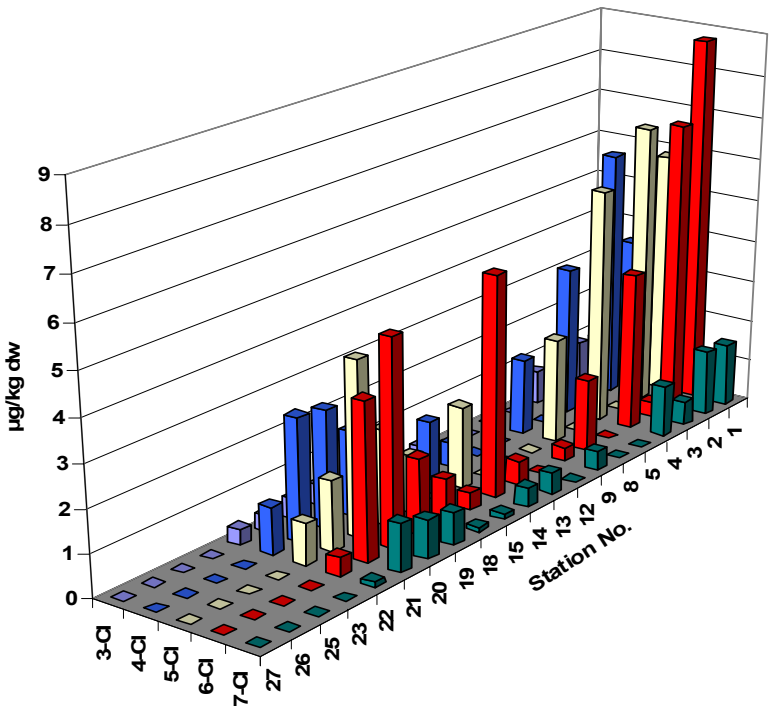


Figure 16: Chlorine based PCB concentrations (µg/kg dw) in surfacial sediments of Abu Qir Bay.

The contribution of PCB congeners based on the number of chlorine atoms in selected sediment samples (stations 1, 2, 4, 8, 13, 14,18, 19, 20 and 21) of Abu Qir Bay, together with the different commercial formulations are shown in **Figure 17**. These samples were selected because of their higher concentrations of PCBs compared to the other samples and thus could give a better indication about the pattern of distribution of the different chlorinated PCBs. These samples also represented the different regions of the bay especially near the major sources of wastewater input into the bay. Taking a close look to **Figure 17**, one can observe the close pattern of distribution between samples collected from the same region as in front and around the Abu Qir Drain represented by stations 1, 2, 20 and 21 and the Maadeya Outlet represented by stations 4, 8 and 14. At the same time, the fact that not all the investigated PCB congeners were detected (below the detection limit) in all the investigated sediment samples could also have an influence when comparing the distribution pattern between different sites. It is thought that the PCB congeners in sea bed sediments closely resemble the parent industrial mixtures unless modified by bacterial mediated degradation (Brown and Wager, 1990). Comparing the composition of PCB in sediments of Abu Qir Bay with that of the different commercial formulations (**Figure 17**), it would be implied that PCBs in Abu Qir Bay have different sources.

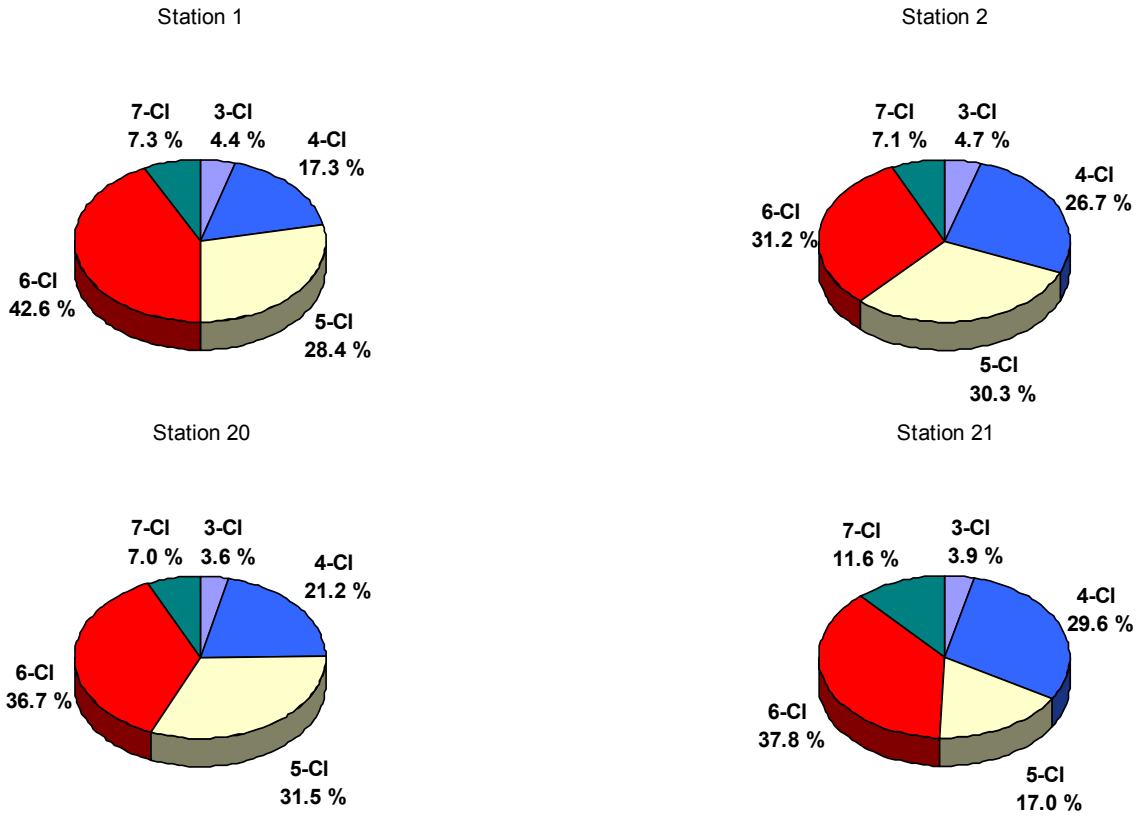
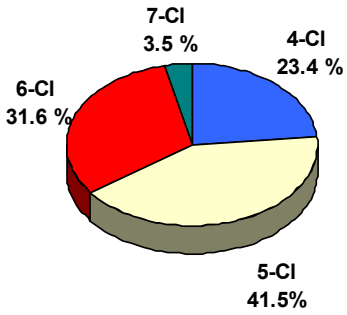
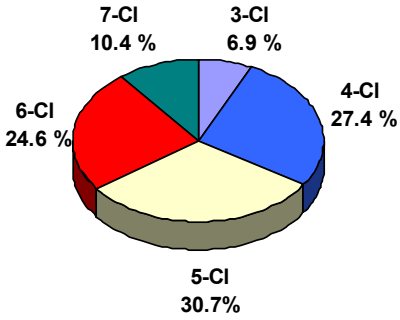


Figure 17: Percent contribution of PCB congeners in selected surfacial sediments of Abu Qir Bay from the Abu Qir Drain region (stations 1, 2, 20 and 21), between the Fertilizer Company and the Electric Power Plant (stations 18 and 19) and the Maadeya region (Stations 4, 8, 13 and 14).

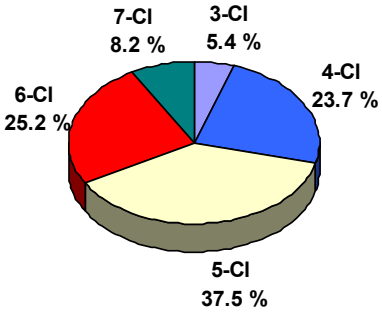
Station 18



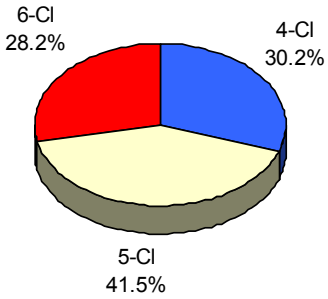
Station 19



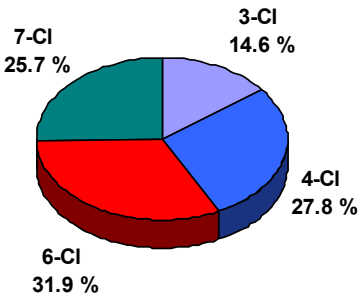
Station 4



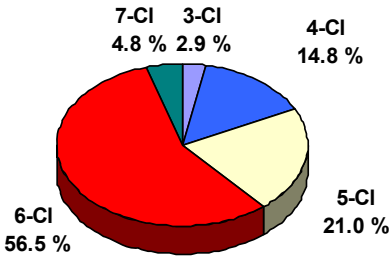
Station 8



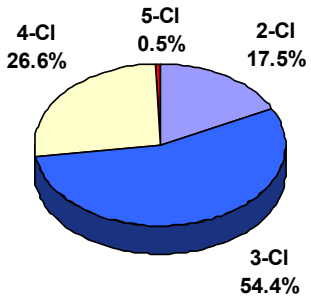
Station 13



Station 14



Aroclor 1016



Aroclor 1242

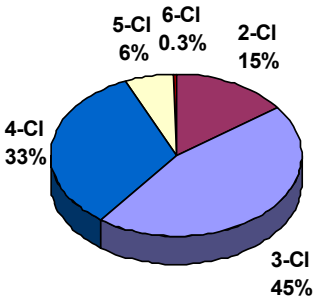


Figure 17. Continued.

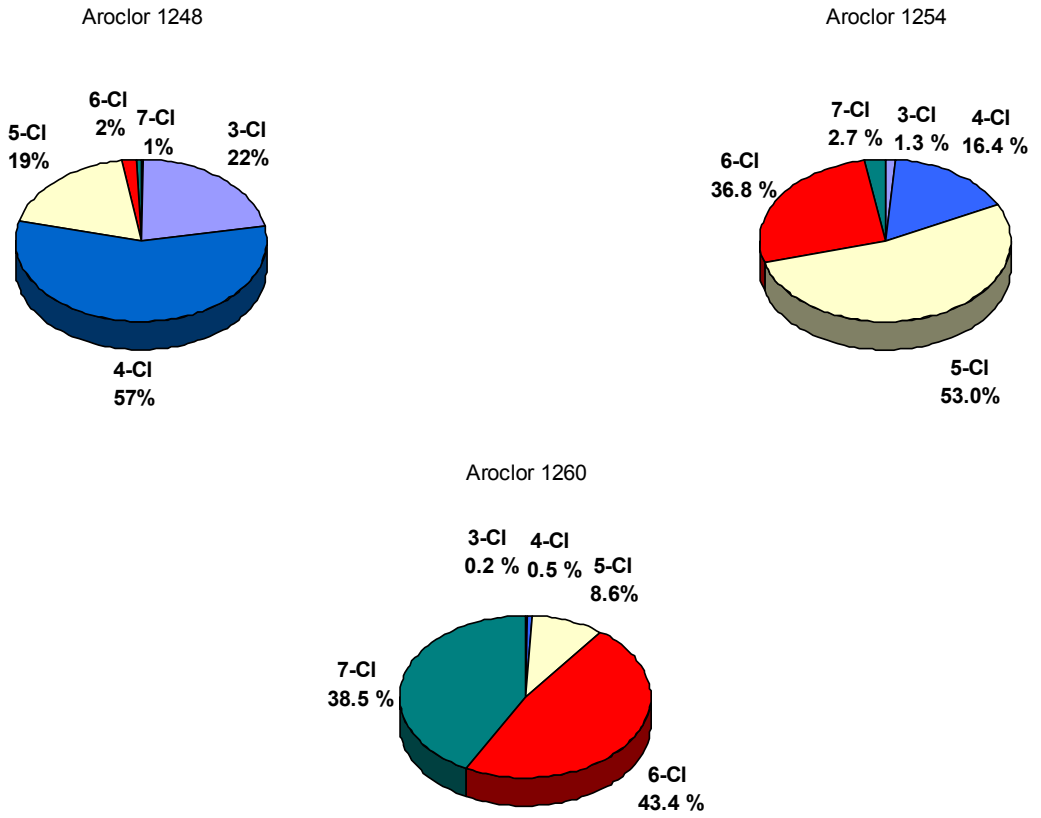


Figure 17: Continued.

3.5. PCBs in the mussel samples of Abu Qir Bay

Concentrations of PCBs recorded in the tissues of both bivalve species are given in **Appendix I, Table A26)**. Concentrations of PCBs in *Mactra corallina* were generally about 10 folds higher than those in tissues of *Tapes decussata* owing to the sample position with respect to the pollution sources in the bay. In *Mactra corallina*, concentrations of the 11 investigated PCB congeners ranged from 0.960 µg/kg dw to 107 µg/kg dw with an average concentration of 43.4 µg/kg dw, whereas in *Tapes decussata*, concentrations ranged from 0.543 µg/kg dw to 10.1 µg/kg dw with an average concentration of 4.65 µg/kg dw. As for the sediments, higher concentrations of the 11 investigated PCB congeners were observed in stations 4, 19 and to a lesser extent 8 and 18 (all representing *Mactra corallin*a) (**Appendix I, Table A26**). Much lower concentrations were observed in stations 27 (*Tapes decussata*) in the western part of the bay and 13 in front of the Wepco Petroleum Company. Very low concentrations of PCBs (< 4 µg/kg dw) were recorded in stations 9, 12, 25 and 26. High significant positive correlation was observed between PCB concentrations in sediments and the mussel samples (r = 0.96).

At the same time significant positive correlation was observed between PCB concentrations and lipid % for both species (r = 0.9 for *Mactra corallina* and r = 0.99 for *Tapes decussata*). In the mussel tissues, PCB 153 and PCB 138 were the most frequently detected congeners being detected in all the investigated samples of *Mactra Corallina*. In *Tapes decussata*, PCB congeners 52, 118, 126 and 156 were completely not detected. PCB 169 was completely not detected in both species. Based on the average detected concentration of each congener in *Mactra corallina*, PCB 118 was the most abundant congener followed by 70, 101, 138, 28, 153, 52, 180 and finally the two coplanar PCB congeners PCB 156 and PCB 126. In *Tapes decussata*, the following order was observed: 153 > 28 > 138 > 180 > 101 > 70. It was noticeable that PCB 118 had the highest concentration between all the other investigated congeners in samples characterized by the highest concentrations of PCBs (stations 4, 8, 18 and 19), whereas PCB 153 was the highest in samples characterized by low degree of contamination with PCBs (stations 9, 12, 13, 25 and 27) (**Appendix I, Table A26**). In the tissue samples of *Mactra corallina*, the contribution of the low chlorinated congeners (3-Cl) to the other PCB congeners is low (**Figure 18**). Although the lower chlorinated biphenyls have an increased mobility from the substrate to water and are therefore more available to aquatic organisms (De Boer et al. 2001), they are very susceptible to metabolism and are eliminated in the marine environment. In *Tapes decussata*, PCB 28 showed slightly elevated contribution from the total PCB especially in station 26, where PCB 28 was the only detected PCB congener, but in both species, tissues were dominated by the higher chlorinated PCB congeners (5 and 6-chlorinated PCB congeners) (**Figure 18**). This is similar to the chlorination pattern of PCBs in the bay sediments, which can explain the high degree of correlation found between PCB concentrations in sediments and mussel tissues precisely *Mactra corallina.* In *Tapes decussata*, the significant contribution from the low chlorinated PCB 28 (17.6 %-100 %) and the undetected PCB concentrations in the sediment associated with this species suggests that PCBs have accumulated in this species from the water column either in the soluble form (PCB 28) or in the particulate form (higher chlorinated PCBs). In addition, the food ingested by these filter feeders is another possible source of contamination with PCBs (Hellou et al. 2002) as higher chlorinated PCB congeners were also detected in *Tapes decussata*. Similar contributions of tetra, penta and hexa chlorinated PCBs were reported for fish species from other worldwide locations (Covaci et al. 2002, Erdogrul et al. 2005; Christoforidis et al. 2008).

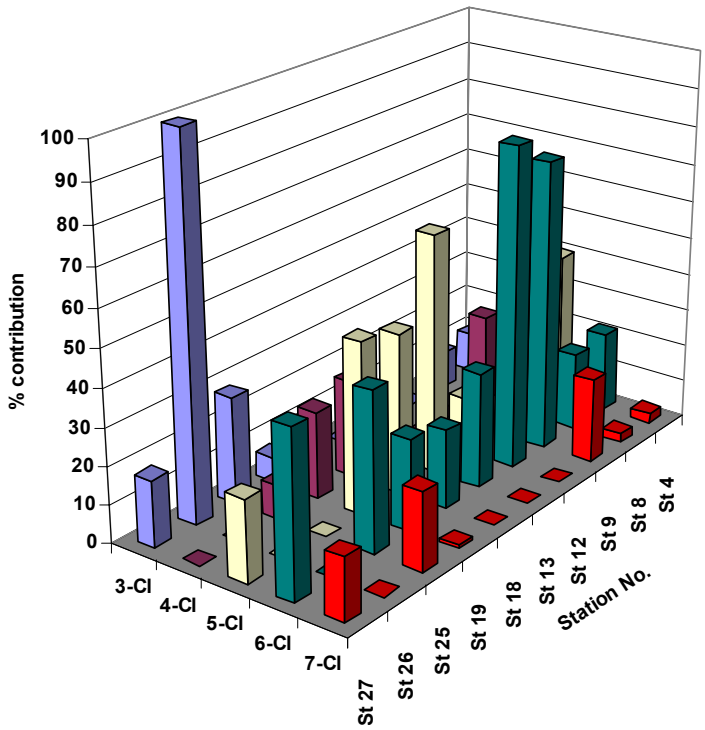


Figure 18: Percent contribution of PCB congeners in mussel tissues based on the number of Cl atoms. Stations 4 to 19 represent *Mactra corallina* and 25 to 27 represent *Tapes decussata*.

Figure 19 shows the detected PCB congeners in sediments and mussel tissues at each location. In sediment samples characterized by relatively higher degree of contamination with PCBs (stations 4, 8, 18 and 19), a quite close pattern of distribution of PCB congeners was also observed in the mussel tissues representing *Mactra corallina*. Significant positive correlation was observed between PCBs in sediments and mussel tissues at these locations (station 4: r = 0.87; station 8: r = 0.878; station 18: r = 0.87; station 19: r = 0.73). For other locations (stations 12, 13), there was a quite different pattern of PCB congener distribution between sediments and their corresponding mussel tissues (*Mactra corallina*) (**Figure 19**). At the same time there was a significant contribution of the lower chlorinated PCB congeners in some of the investigated mussel samples (stations 8 and 18), which was not marked in their corresponding sediments. Also some of the more toxic coplanar PCB congeners (PCB 126 and 156) were recorded in the mussel tissues of some samples (stations 18 and 19) at the same time they were not found in the corresponding sediment samples (**Figure 19**). Bioaccumulation has been discussed relative to the structure of PCBs, where it was deduced that coplanar congeners accumulate more from water than through the food chain (Willman et al. 1999).

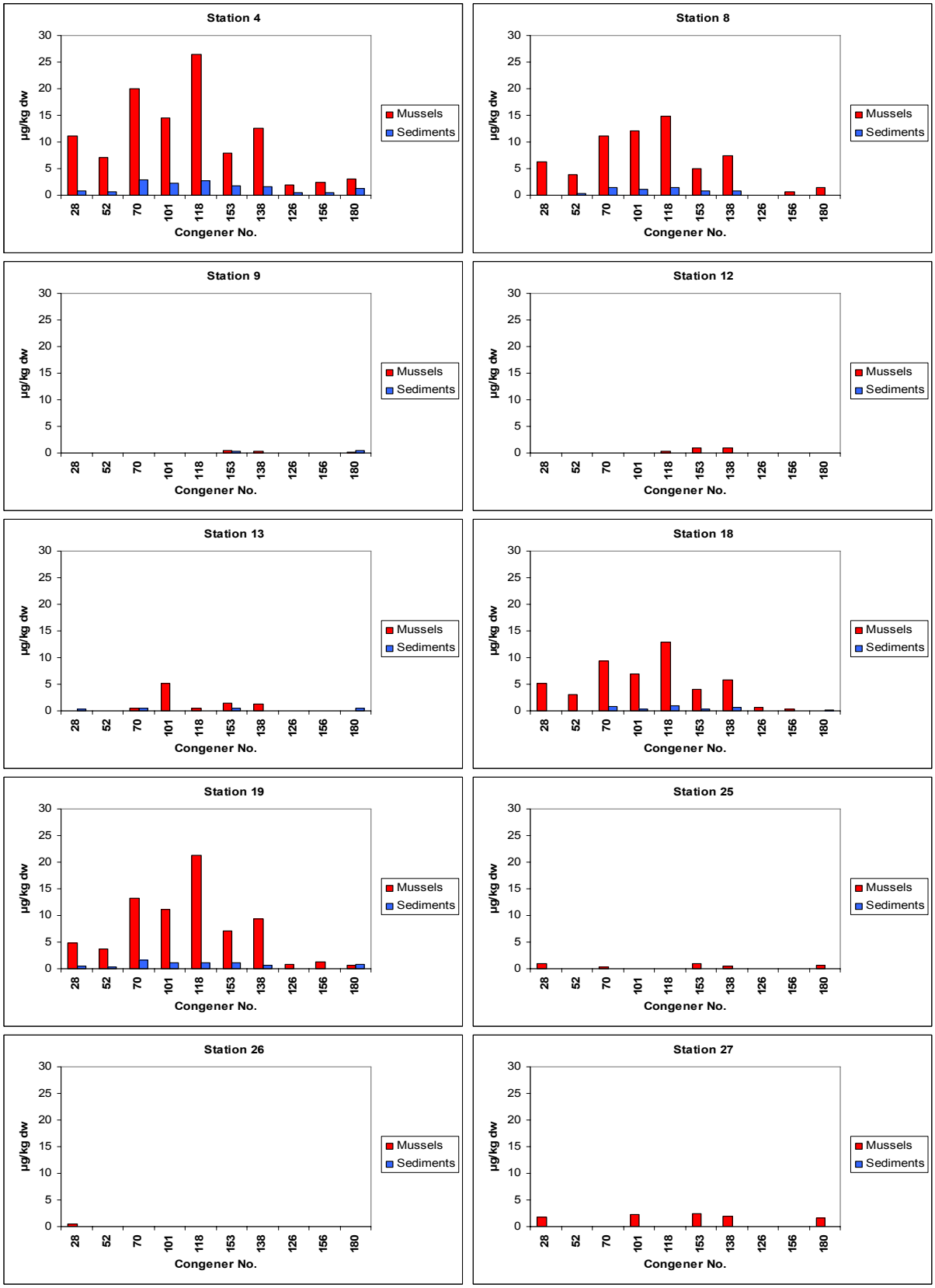


Figure 19: Distribution of PCB congeners in sediment samples and mussel tissues of Abu Qir Bay.

3. 6. Organochlorine pesticides and chlorpyrifos in Abu Qir Bay sediments

3.6.1. DDT and its metabolites (DDTs)

DDTs were detected in 85 % of the investigated sediment samples but their contribution of individual metabolites showed differences. DDTs were completely not detected at station 23 and stations 25 and 26 in the western part of the bay. p,p'-DDE was the only detected isomer in the reference site (station 5). Similar to PCBs, high concentrations of DDTs were recorded in the bay sediments especially at stations influenced by the industrial, agricultural and domestic wastewater discharged from Abu Qir Drain (stations 1, 2, 20 and 21), in front of the Maadeya Outlet (station 4) and stations which could be influenced by the water discharged from the Maadeya Outlet as a result of the circulation pattern in the bay (Stations 12, and 14) (**Figure 20**). The concentrations of total DDTs in sediments varied from <DL to 128 µg/kg dry weight (station 1) with an average concentration of 26.5 µg/kg dry weight (**Appendix I, Table A27**). p,p´-DDE was the most abundant isomer been detected in 85 % of the sediment samples followed by o,p´-DDD (80 %), p,p´-DDD (70 %), p,p'-DDT (40 %), o,p'-DDE (30 %) and finally o,p´-DDT, which was detected only in 25 % of the sediment samples. Concentrations of DDD and DDE isomers were much higher compared to the DDT in almost all stations except stations 18 and 27 (**Figure 21**). Concentrations of DDTs in the bay sediments generally decrease in the offshore direction except the nearshore-offshore profile in front of Wepco Petroleum Company. Based on the average concentrations, DDTs are in the following order of predominance: p,p´-DDD > o,p´-DDD > p,p´-DDE > o,p´-DDE > p,p´-DDT > o,p´-DDT.

Concentrations of DDTs in the bay sediments are considered as a reflection of the intensive application of DDT in Egypt, especially for agricultural purposes. The high concentrations of total DDTs in these sediments compared to concentrations worldwide indicate that DDT usage was heavy and the bay has received significant inputs of DDTs. Two major sources may be responsible for the elevated concentrations of DDTs in the bay sediments: the Abu Qir Drain, which discharges large amounts of agricultural wastes from the large cultivated lands in the region, in addition to toxic industrial wastes and the Maadeya Outlet, which discharges the water of Lake Edku known to be polluted with agricultural wastes.

In the northwestern part of the bay (station 27), only p,p'-DDT and p,p'-DDE were detected. The detection of DDTs at this site could possibly be related to the storm water runoff and residential wastes directly discharged into the bay. Similar assumption was obtained by Barakat et al. (2002) in his investigation on the contamination of the Western Harbour sediments with organochlorine compounds.

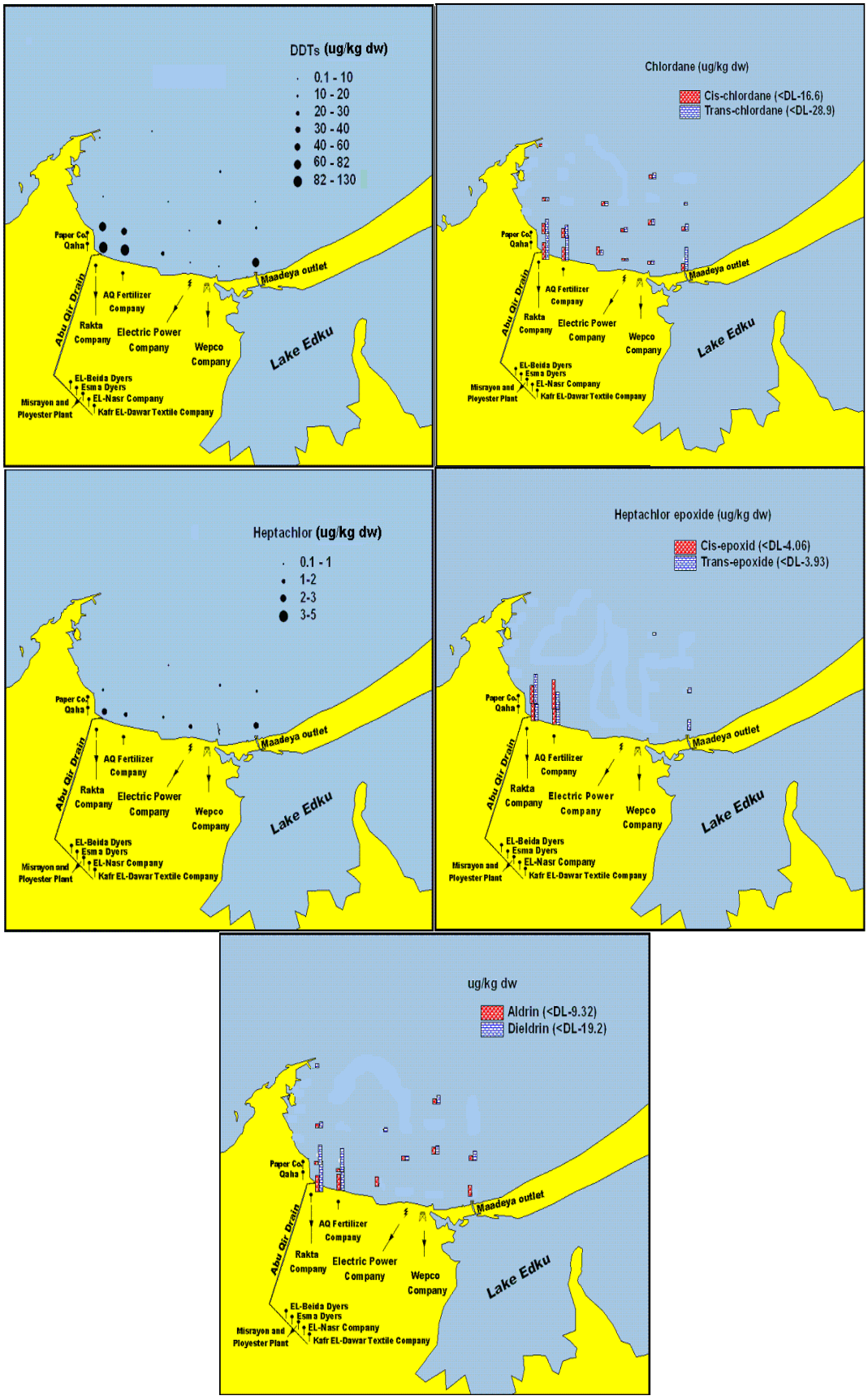


Figure 20: Spatial distribution of organochlorine pesticides in surfacial sediments of Abu Qir Bay.

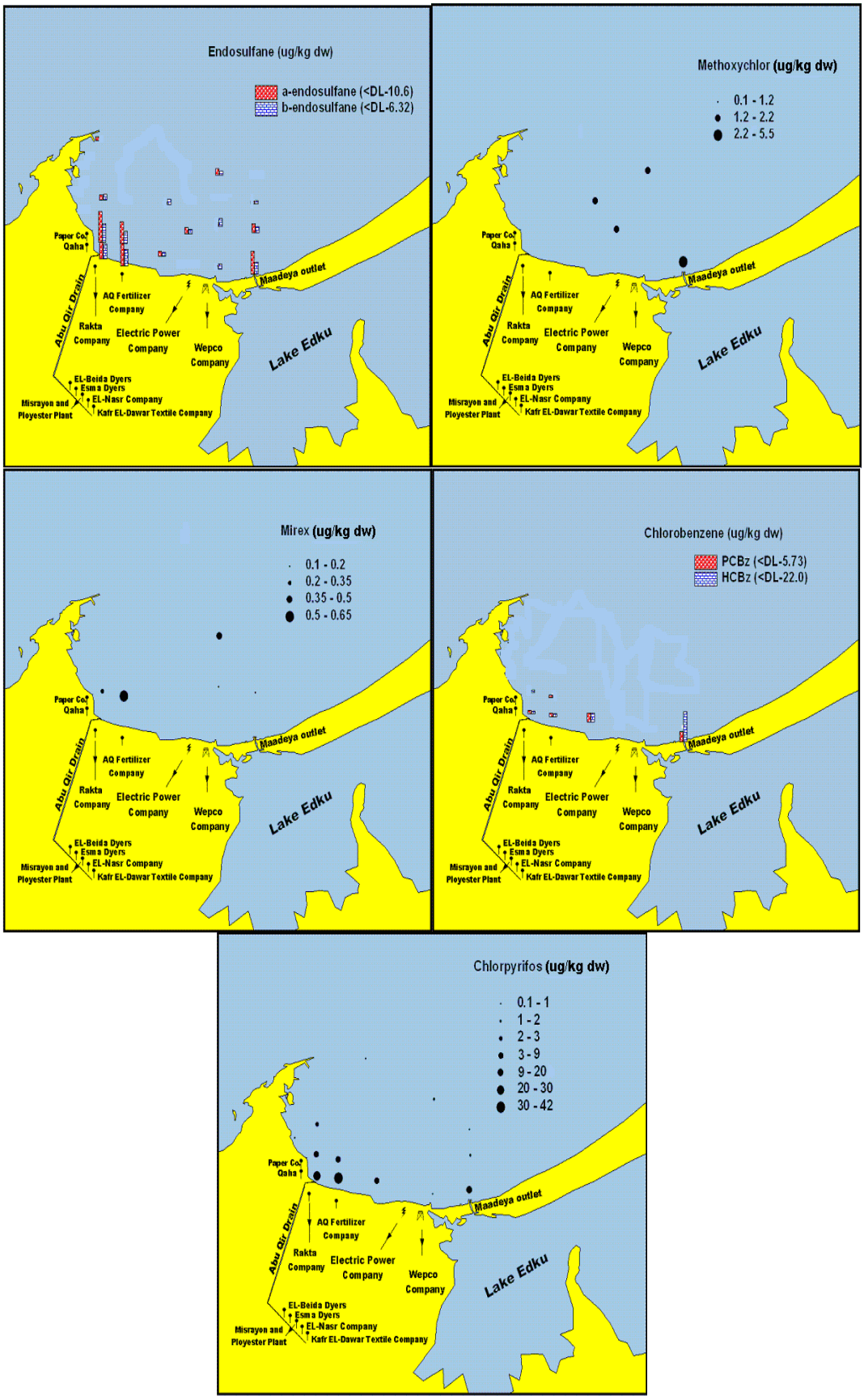


Figure 20. Continued.

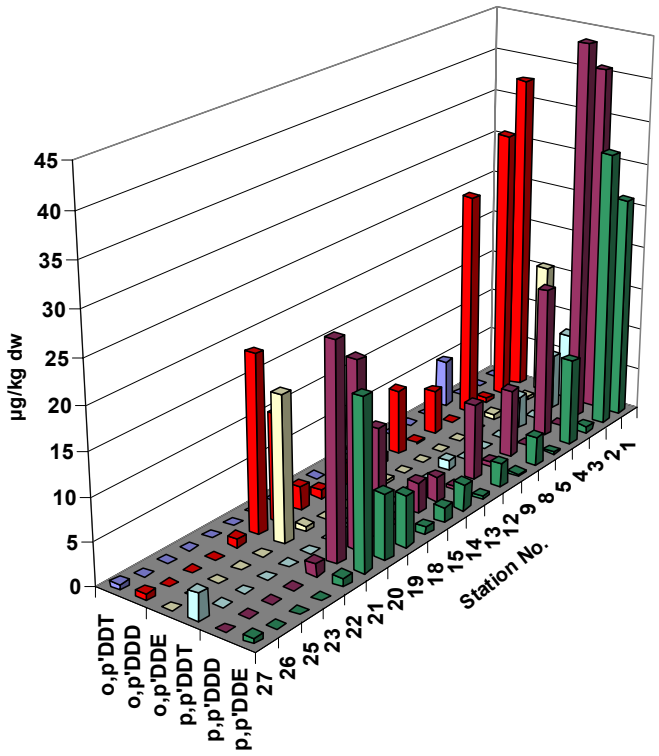


Figure 21: Distribution of DDT and its metabolites in surfacial sediments of Abu Qir Bay.

The composition of organochlorines and their metabolites can provide some information for a better understanding of the origin and transport of these contaminants in the environment. Peng et al. (2005) reported a possibility of the continuous illegal use of DDT in China using the ratio of (DDD + DDE)/∑DDTs. DDT undergoes degradation to DDD and DDE in the natural environment by chemical and biological processes (Wedemeyer, 1967; Baxtor, 1990; Barakat et al. 2002). Under aerobic conditions, DDT is dehydrochlorinated to DDE by soil microorganisms (Burge, 1971; Matsumura and Benezet, 1978; Tolosa et al. 1995; Lee et al. 2001) or through photochemical reactions in the presence of sunlight (Maugh, 1973) and through dehydrochlorination in bacteria (Pfaender and Alexander, 1972) and animals (Kurihara et al. 1988). DDE is recalcitrant and does not readily degrade in the environment. Under anaerobic and reducing conditions, DDT is degraded by microorganisms (reductive dechlorination; Wedemyer, 1967; Patil et al. 1972; Albone et al. 1972) and abiotically by iron prophyrins to DDD (Castro, 1964; Zora et al. 1974; Baxtor, 1990). DDD can be further metabolized to DDMU and other degradation products (MacGregor, 1976; Matsumura and Benezet, 1978). Microbial degradation of DDT, DDD and DDE is generally slow, resulting in environmental persistence of these compounds. **Figure 22** shows the percent contribution of DDT (o,p´-DDT + p,p´-DDT) and its metabolites. Over 70 % of the total DDTs in sediments from stations 1, 2, 4, 12, 13, 14, 15 and 19 and all the DDTs observed in sediments from stations 3, 8, 9, 20, 21 and 22 are present as DDT metabolites (DDD and DDE). DDTs are therefore not newly released into those locations and were mainly present as metabolites (aged DDTs). Only stations 18 and 27 show higher contribution of p,p'-

DDT which may indicate slow degradation of DDT or recent inputs of fresh DDTs at these locations (Tavares et al. 1999; Yuan et al. 2001). DDD accounted for the majority of DDT related compounds at these locations (**Figure 22**). This indicates that the reductive dechlorination of DDT to DDD under anaerobic conditions was the main degradation pathway of DDT in the bay sediments (Wedemeyer, 1967; Baxtor, 1990). DDE isomer dominated only at stations 3 which may be a consequence of a more aerobic milieu at this nearshore location.

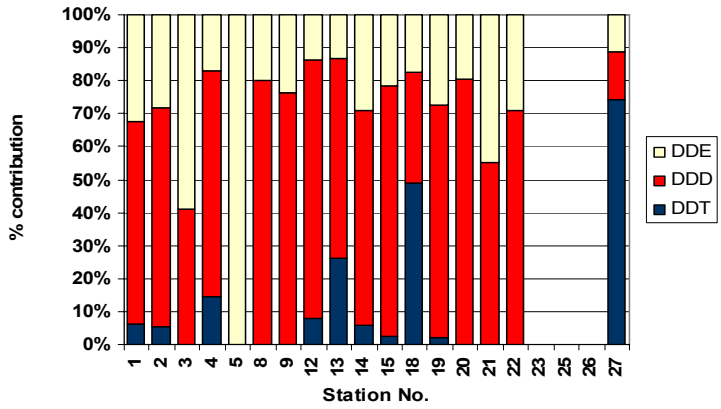


Figure 22: Percent contribution of DDT and its metabolites (DDD and DDE) in surfacial sediments of Abu Qir Bay.

DDT was widely used in Egypt on a variety of agricultural crops and for the control of disease vectors. The largest agricultural use of DDT has been on cotton, which accounted for more than 80 % of the use before its ban. Although its usage was banned in 1988 (Barakat et al. 2002), its detection along with the detection of its breakdown products in sediments is expected because the reported environmental half life of DDTs is estimated as 10 to 20 years (Woodwell et al. 1971; Sericano et al. 1990).

3.6.2. Hexachlorocyclohexane (HCHs)

Concentrations of the hexachlorocyclohexane (HCH) (α, β, γ and δ) isomers ranged from <DL to 34.5 µg/kg dw with an average concentration of 7.56 µg/kg dw (**Appendix I, Table A27**). Higher concentrations of the HCH isomers were observed in stations 2, 1, 20, 21, which are affected by the wastewater discharged from the Abu Qir Drain (**Figure 20**). In addition, high concentration was also observed in station 4 in front of Lake Edku. Detected concentrations of the HCH isomers generally decrease in the offshore direction. HCH isomers were detected in most of the investigated sediment samples but with different contributions (**Figure 23**). γ-HCH was the most frequently detected isomer been detected in 70 % of the sediment samples followed by δ-HCH (60 %), α-HCH (55 %) and finally β-HCH (30 %). Based on the average concentrations, the isomers appeared in the following descending order: γ-HCH > α-HCH > β-HCH > δ-HCH.

Detected concentrations of HCH isomers in the bay sediments were much lower than their corresponding DDTs concentrations. This could be attributed to the tendency of HCH isomers to metabolize after some years to pentachlorocyclohexane, tetrachlorobenzene and other compounds (Dannenberger and Lerz, 1998) and/or the higher solubility of HCH isomers compared to DDTs (Dannenberger and Lerz, 1994). HCH isomers have higher water solubility in seawater (8 mg/L for γ-HCH, Weil et al. 1979) and a lower affinity to suspended particulate matter than chlorinated phenyls and DDTs (0.007 mg/L for both PCB 110 and p,p´DDT, Weil et al. 1979). As a consequence, their removal from the water column by particle association and sedimentation is slower and the concentrations in the water column are expected to be kept at a higher level. The water solubility, expressed as octanol-water partition coefficients (K_{ow}), is a key parameter in assessing the potential environmental behaviour of lipophilic compounds. The log value of octanol-water partition coefficient for DDT and PCB are higher than those of HCH isomers (log K_{ow} for p,p´-DDT is 5.13, 6.83 for PCB 138 and 4.14 for HCH isomers) (Rapaport and Eisenreich, 1984; Hawker and Connell, 1988; http://www.epa.gov/opptintr/exposure/pubs/episuite.htm).

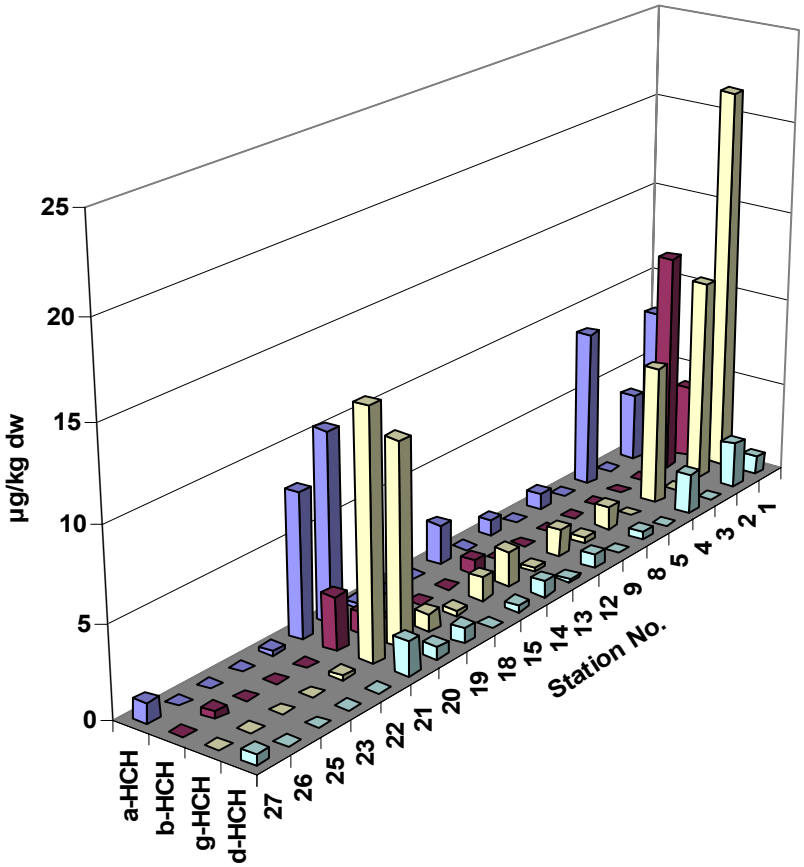


Figure 23: Isomeric concentrations of HCHs in surfacial sediments of Abu Qir Bay.

The isomeric contribution of HCH in the bay sediments as shown in **Figure 24** was not uniform. It can be generally seen that γ-HCH was the dominant isomer in 77 % of the samples where this isomer was detected and its percent contribution ranged from 33.1 % to 76.7 %. In addition, it was the only

detected isomer in stations 9 and 18. α-HCH isomer came in the second order after γ-HCH in most of the investigated samples with percent contribution ranging from 12.6 % to 65.9 %. In addition, this isomer was the dominant isomer in stations 4 and 27 (**Figure 24**). Based on the average values of percent contribution of each isomer, they can be arranged according to the following descending order: γ-HCH > α-HCH > δ-HCH > β-HCH. Thus we can conclude that both γ and α isomers were the most dominant isomers in sediments of Abu Qir Bay. Both isomers also dominated the sediments and biota from the Danube Delta, Romania (Covaci et al. 2006)

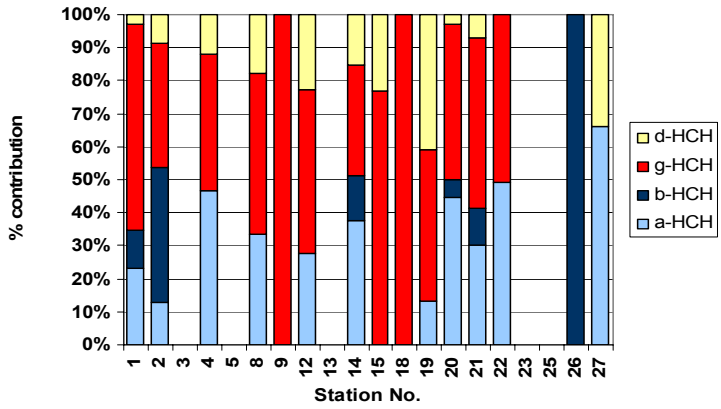


Figure 24: Percent contribution of HCH isomers in surfacial sediments of Abu Qir Bay.

For the technical HCH mixtures, the relative proportions of the four major components were α (65-70 %) > γ (12-14 %) > δ (6 %) and β (5-6 %). Lindane consists of 99 % γ-HCH. The ratio of α-HCH/γ-HCH in the sediments is 4.6 to 5.8 (Zhang et al. 2004) or 4 to 15 (Wurl and Obbard, 2005) for technical HCHs mixtures and between 0.2 and 1 for the pesticide lindane (McConnell et al. 1998). These ratios are expected to increase with distance from the source (Ramesh et al. 1989), assuming the transformation of γ-HCH to α-HCH. Calculated values of α-HCH/γ-HCH ratio in sediments of Abu Qir Bay ranged from 0.285-1.14 indicating lindane as the main HCH source. This agrees with the data given by EL-Sebae, (1989), that lindane was intensively used in Egypt in the period from 1952 to 1978. About 11300 t were used in agriculture. No data are available for the use of lindane or HCHs in Egypt after this time period.

3.6.3. Cyclodiene pesticides

cis-Chlordane, trans-chlordane, heptachlor, cis-heptachlor epoxide, trans-heptachlor epoxide, aldrin, dieldrin, α-endosulfane, β-endosulfane and mirex were the investigated cyclodiene pesticides in surfacial sediments of Abu Qir Bay. Concentrations are summarized in **Appendix I, Table A28** and presented in **Figure 25**. Chlordanes (cis and trans) and β-endosulfane were the most frequently detected cyclodiene pesticides in sediments of Abu Qir Bay, where they were detected in 70 % of the investigated samples followed by dieldrin (60 %), aldrin and α-endosulfane (55 %), heptachlor (50 %), trans-heptachlor epoxide (35 %), mirex (25 %) and finally cis-heptachlor epoxide, which was detected in only 20 % of the investigated sediment samples. According to the calculated average concentrations, cyclodienes can be arranged according to the following descending order: trans-

chlordane (6.28 µg/kg dw) > dieldrin (3.72 µg/kg dw) > cis-chlordane (3.46 µg/kg dw) > α-endosulfane (2.54 µg/kg dw) > aldrin (1.83 µg/kg dw) > β-endosulfane (1.54 µg/kg dw) > heptachlor (0.973 µg/kg dw) > trans-heptachlor epoxide (0.666 µg/kg dw) > cis-heptachlor epoxide (0.577 µg/kg dw) > mirex (0.0866 µg/kg dw). Cyclodiene pesticides were below the detection limit in stations 5, 23, 25 and 26. Most of the cylcodiene pesticides were not detected in the western part of the bay except for cis-chlordane, α-endosulfane and dieldrin in station 27 in the northwestern part of the bay (**Figure 20**).

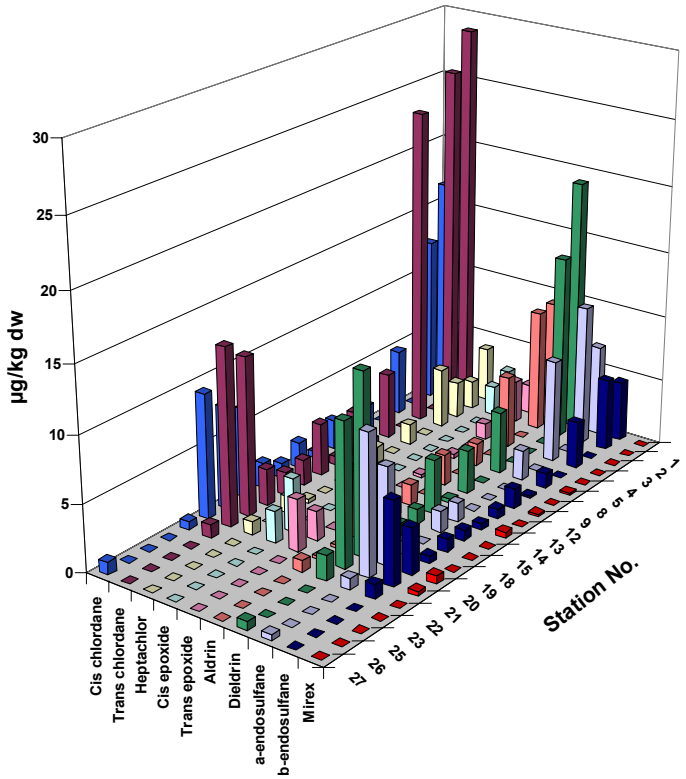


Figure 25: Concentrations of cyclodiene pesticides (µg/kg dw) in surfacial sediments of Abu Qir Bay.

Concentrations of cyclodiene pesticides were generally higher in front of the Abu Qir Drain (stations 1, 21) and the Fertilizer Company (stations 2, 20) and to a lesser extent in front of the Maadeya Outlet (station 4) (**Figure 20**) as the majority of the investigated pollutants in the present study. Concentrations of trans-chlordane were generally higher than cis-chlordane in the majority of the sediment samples **(Figure 25**). This is expected as the concentration of the trans-isomer in the technical mixture is higher than the cis-isomer (Dearth and Hites, 1991; Barakat et al. 2002) which was intensively applied in Egypt in 1985 (EL-Sebae, 1989). About 50 t of formulated chlordane was used in Egypt during this year. According to the UNEP, the use of chlordane is severely restricted to non-agricultural uses in Egypt.

Heptachlor showed the maximum concentration (4.51 µg/kg dw) in front of the Maadeya Outlet (station 4). At the same time, the highest concentrations of cis- (4.06 µg/kg dw) and trans- (3.93 µg/kg dw)

heptachlor epoxides were observed in stations 20 and 21 respectively in the region affected by the water discharged from the Abu Qir Drain. Concentrations of heptachlor and its epoxides (cis and trans) were much lower than chlordane concentrations in sediments of Abu Qir Bay. Concentrations of heptachlor observed in stations 1 and 4 (4.14 µg/kg dw and 4.51 µg/kg dw respectively) were higher than concentrations in the rest of the bay. At the same time, cis-heptachlor epoxide was only detected in front of the Abu Qir Drain (stations 1, 21) and the Fertilizer Company (stations 2, 20) (**Figure 20**). As for the trans-isomer, concentrations were higher in front of the Abu Qir Drain and the Fertilizer Company compared to concentrations in front of the Maadeya (stations 4, 8 and 12). The low detected concentrations of heptachlor and its epoxides in sediments of Abu Qir Bay may suggest that the detected heptachlor is due to the application of the chlordane technical mixture which includes heptachlor as one of its components (Parlar et al. 1979; Miyazaki et al. 1983). The occurrence of heptachlor epoxides in sediments of Abu Qir Bay can be attributed to the microbial transformation of the heptachlor (parent compound) by epoxidation (ATSDR, 1993).

Concentrations of aldrin and dieldrin were generally relatively low in sediments of Abu Qir bay (close to the heptachlor concentrations) except in stations 1, 2 and 4 for aldrin and 1, 2, 20 and 21 for dieldrin, where obviously higher concentrations were determined (**Figure 20**). Concentrations of aldrin ranged from <DL to 9.32 µg/kg dw with an average concentration of 1.85 µg/kg dw, whereas concentrations of dieldrin ranged from <DL to 19.2 µg/kg dw with an average concentration of 3.72 µg/kg dw. Concentrations of dieldrin were generally higher than aldrin in most of the sediment samples. This could be attributed to the fact that aldrin is converted into dieldrin in the sediments by epoxidation. At the same time, dieldrin is known to be more persistent than aldrin.

Concentrations of α-endosulfane were generally higher than β-endosulfane, which can be related to the higher contribution of the α-isomer in the technical mixture (the ratio of α-endosulfane to β-endosulfane is about 7: 3) (Shetty et al. 2000). At the same time it was found that β-endosulfane can be converted into α-endosulfane (Schmidt et al. 1997, 2001). Concentrations of α-endosulfane ranged from <DL to 10.6 µg/kg dw with an average concentration of 2.53 µg/kg dw, whereas concentrations of β-endosulfane ranged from <DL to 6.3 µg/kg dw with an average concentration of 1.54 µg/kg dw (**Appendix I, Table A28**).

Mirex was rarely detected in Abu Qir Bay as it was detected in only five sediment samples at very low concentrations (**Figure 20**) compared to the other cyclodiene pesticides, DDTs and HCH isomers. Concentrations generally ranged from <DL to 0.616 µg/kg dw with an average concentration of 0.087 µg/kg dw. Unlike all the other investigated organochlorine pesticides, mirex was not detected in the nearshore stations, which showed maximum concentrations of most of the investigated organochlorine pesticides (**Figure 20**).

3.6.4. Methoxychlor, PCBz and HCBz

Methoxychlor was detected in 25 % (<DL-5.16 µg/kg dw) of the investigated sediment samples with slight variations between sites except in station 4 in front of the Maadeya Outlet where the highest concentration was recorded (**Figure 20**).

Concentrations of PCBz and HCBz in sediments of Abu Qir Bay were below detection limit or very low except in station 4 and station 19 (**Appendix I, Table A29**). This may reflect the limited sources of chlorobenzenes in the Abu Qir region. Elevated concentrations of HCBz in front of Maadeya Outlet could be attributed to the agricultural discharges from Lake Edku. At the same time, the relatively high concentration of HCBz in station 19 could possibly be related to the presence of a direct discharge of industrial water effluents close to the sample location. The detected concentrations of PCBz could be due to the degradation pathway of HCBz in the bay sediments. The presence of a high significant positive correlation between concentrations of PCBz and HCBz in the bay sediments supports this assumption ($r = 0.88$ at $p < 0.05$).

3.6.5. Chlorpyrifos

Chlorpyrifos was the only investigated organophosphorus pesticide in sediments of Abu Qir Bay. It was selected because it was previously detected in sediments along the Coast of Alexandria. Also chlorpyrifos is very highly toxic for aquatic organisms (Pait et al. 1992). Concentrations ranged from <DL to 41.7 µg/kg dw with an average concentration of 5.92 µg/kg dw (**Appendix I, Table A29**). Chlorpyrifos was detected in 65 % of the investigated sediment samples. The highest detected concentration of chloropyrifos was observed in station 2 in front of the Fertilizer Company (**Figure 20**). At the same time, concentrations recorded in sediments, located in front of the Abu Qir Drain (station 1: 29.6 µg/kg dw) and the Maadeya Outlet (station 4: 17.4 µg/kg dw) were much higher than concentrations detected in the rest of the bay. Based on the average concentrations, chlorpyrifos came in the fourth order after p,p'-DDD (9.42 µg/kg dw), o,p'-DDD (7.84 µg/kg dw) and trans-chlordane (6.28 µg/kg dw). This can be attributed to the dependence on organophosphorus pesticides in agricultural purposes after banning the use of organochlorine pesticides. According to EL-Sebae, (1989), 13500 t of chlorpyrifos were used in Egypt in the period from 1969-1985.

3.6.6. Influence of the physicochemical properties of the bay sediments on the spatial distribution of the organochlorine pesticides in Abu Qir Bay.

Chlorinated organic compounds are associated with suspended particles, which may sink and act as a contaminant source to sediments (Dachs et al. 1996). A portion of the hydrophobic organochlorine compounds in surface seawater associated with biotic and abiotic macroparticles, and then is removed from the surface to benthic layers by the settling of these particles into the water column. In this context, the sediments are regarded as being a part of an ultimate sink of the hydrophobic and persistent toxic compounds (Iwata et al. 1994). In sediments, it is the organic carbon fraction which is responsible for the accumulation of the organochlorine compounds because of their lipophilic

character (high organic carbon partition coefficient). Correlation coefficients based on the relationship between concentrations of the investigated chlorinated organic pollutants and TOC and clay contents of the bay sediments are summarized in **Appendix II, Table 2**.

Significant positive correlation was observed between TOC content and each of DDTs, HCHs, cis-heptachlor epoxide, α-endosulfane and β-endosulfane in sediments of Abu Qir Bay (r ranged from 0.7 to 0.87). Moderate correlation was observed in the case of cis-chlordane, trans-chlordane, total chlordane, dieldrin and chlorpyrifos (r ranged from 0.58 to 0.7). Weak or no correlation was observed for all the other investigated chlorinated organic compounds ($r < 0.58$).

Significant positive correlation was also observed between the clay content and each of DDTs, cis-heptachlor epoxide, β-endosulfane, trans-chlordane, total chlordane and chlorpyrifos ($r > 0.7$) in the bay sediments. Moderate correlation was observed in the case of HCHs, α-endosulfane and cis-chlordane (r ranged from 0.6 to 0.7) and weak or no correlation for the rest of the investigated chlorinated organic compounds ($r < 0.6$).

It can be observed from the obtained values that the behaviour of the organochlorine pesticides was greatly variable and that the TOC content of the bay sediments can partly affect the spatial distribution of some chlorinated organic pollutants, in addition to the distance from the source, which was demonstrated by the highest concentrations of the majority of the investigated chlorinated organic pollutants in the nearshore stations affected by direct wastewater discharges. However, it must be pointed out that the occurrence of most of the investigated organochlorine pesticides below the limit of detection in most of the sediment samples greatly affected the degree of correlation.

3. 6.7. Comparison between concentrations of chlorinated organic pollutants in Abu Qir Bay sediments with concentrations worldwide

Concentrations of PCBs recorded in the present work were much lower than concentrations observed in the Mediterranean Sea sediments and in other coastal sediments in different geographical positions except for the northwestern basin of the Mediterranean Sea and the Western Baltic Sea (**Figure 26** and **Appendix I, Table A30**). At the same time detected concentrations of DDTs in the bay sediments in the present study were lower than concentrations previously recorded in the Mediterranean Sea coastal sediments, but higher than concentrations recorded in other coastal sediments worldwide (**Appendix I, Table A30)**. Concentrations of PCBs, DDTs and HCHs recorded in the present work were generally lower than concentrations previously recorded in sediments of Abu Qir Bay and in other coastal areas along the coast of Alexandria (**Figure 26** and **Appendix I, Table A30**). Detected concentrations of chlordanes in the present work were higher than concentrations recorded in coastal sediments of Egypt (**Figure 26**). Chlorpyrifos and endosulfane showed lower concentrations in the present work compared to sediments of Alexandria Harbour (**Appendix I, Table A30**).

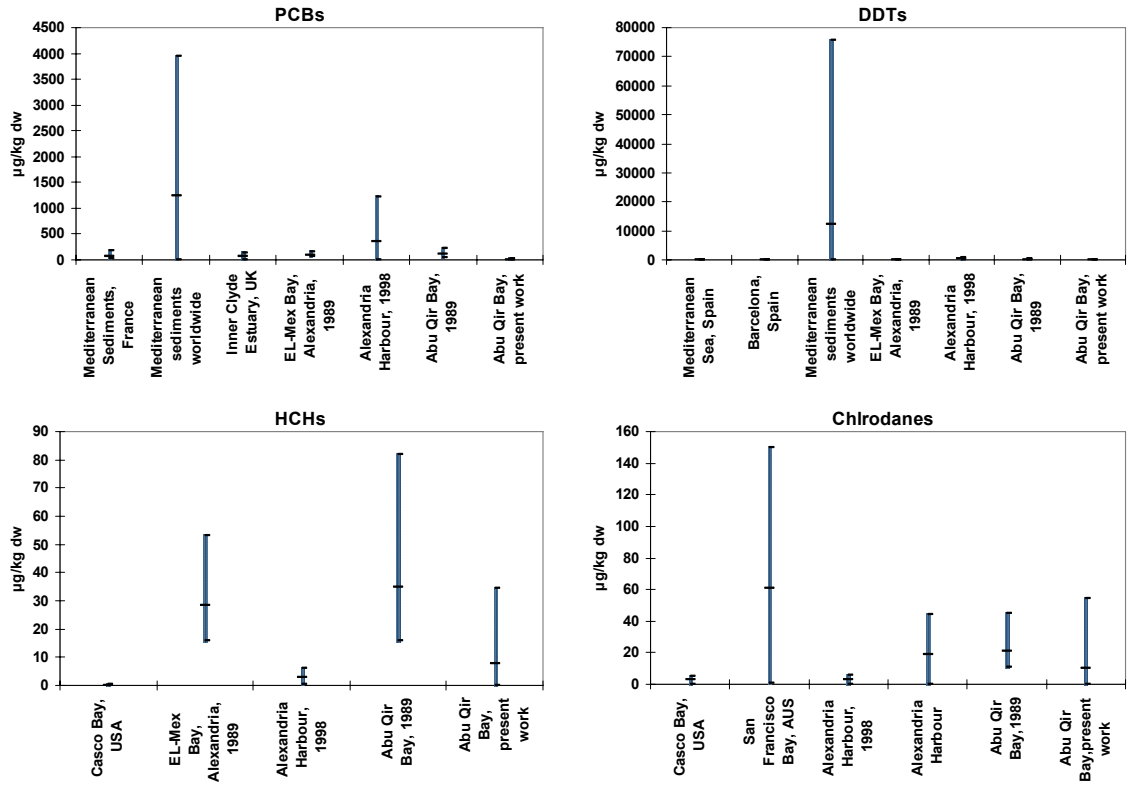


Figure 26: Ranges and average concentrations of PCBs and organochlorine pesticides (µg/kg dw) in surfacial sediments worldwide, along the Egyptian Coast and previously performed on Abu Qir bay compared to the present work.

Detected concentrations of organochlorine pesticides in sediments of Abu Qir Bay are generally high compared to concentrations observed in other parts of the world except in some severely contaminated locations such as sediments of San Francisco Bay, California, and Saronikos Gulf, Greece, and some severely contaminated sites along the Mediterranean Sea. In comparison, the contamination of sediments in Abu Qir Bay by DDTs, HCHs and chlordanes appeared to be high on worldwide basis.

3.7. Organochlorine pesticides in the mussel samples of Abu Qir Bay

Concentrations of organochlorine pesticides in the mussel samples are shown in **Appendix I, Table A31**. Most of the investigated pesticides, which were detected in the sediment samples, were observed in *Mactra corallina*, whereas only heptachlor, p,p'-DDE, p,p'-DDD and chlorpyrifos were recorded in *Tapes decussata*. Aldrin, o,p'-DDT, p,p'-DDT and β-HCH were completely absent in both species. The absence of aldrin, o,p'-DDT and p,p'-DDT can be related to the metabolic activity of the bivalve species. Based on the average concentrations of the detected pesticides in *Mactra corallina*, they can be arranged in the following descending order: DDTs (14.1 µg/kg dw) > chlordanes (8.93 µg/kg dw) > chlorpyrifos (8.13 µg/kg dw) > HCHs (3.94 µg/kg dw) > dieldrin (2.77 µg/kg dw) > endosulfane (2.02 µg/kg dw) > methoxychlor (1.17 µg/kg dw) > trans-epoxide (0.690 µg/kg dw) > heptachlor (0.498 µg/kg dw) > cis-epoxide (0.200 µg/kg dw) > mirex (0.193 µg/kg dw). In *Tapes decussata*, DDTs were much higher than detected concentrations of chlorpyrifos and heptachlor

(**Appendix I, Table A31**), which is attributed to the more bioaccumulative ability of DDTs. For most of the investigated pesticides, higher concentrations were always observed in stations 4 and 8 in front of the Maadeya Outlet and station 18.

DDTs were detected in all the investigated samples with concentrations ranging from 0.944 µg/kg dw (station 26) to 31.3 µg/kg dw (station 8). The DDT distribution in the mussel samples was different to that of the sediments. The mussel samples had higher levels of p,p'-DDE compared to the sediment samples, where DDD was the main transformation product (**Figure 27**). p,p'-DDE represented from 48.7 % to 100 % of the total detected DDTs in both species. Several authors have observed preferential accumulation of DDT degradation products in aquatic organisms (Boon and Eijgenraam, 1988; Colombo et al. 1995, 1997; Kammann et al. 1992; Thompson et al. 1999; Qiang, 2004; Sapozhnikova et al. 2004). This phenomenon is due to uptake, metabolism and depuration mechanisms for DDT compounds in mussels (Sericano, 1990; Qiang, 2004). Indeed, bivalves have a certain capacity to metabolize organic contaminants (Livingstone, 1994).

Chlordanes (cis and trans isomers) ranged from <DL to 31.7 µg/kg dw in the mussel samples. cis Chlordane was only detected in two samples (stations 4, 8), whereas trans-chlordane was detected in all the samples of *Mactra corallina* (**Appendix I, Table A31**). Like in sediments, concentrations of the trans-isomer were higher than the cis-isomer. High significant positive correlation was observed between concentrations of chlordanes in the sediments and the mussel samples (r =0.9).

Chlorpyrifos, like DDTs and chlordanes, was detected in relatively high concentrations in *Mactra corallina* (**Appendix I, Table A31**). This organophosphate pesticide was detected in only one sample of *Tapes decussata* (station 27) but with a much lower level than concentrations recorded in tissues of *Mactra corallina*. Concentrations generally ranged from, DL to 15.0 µg/kg dw.

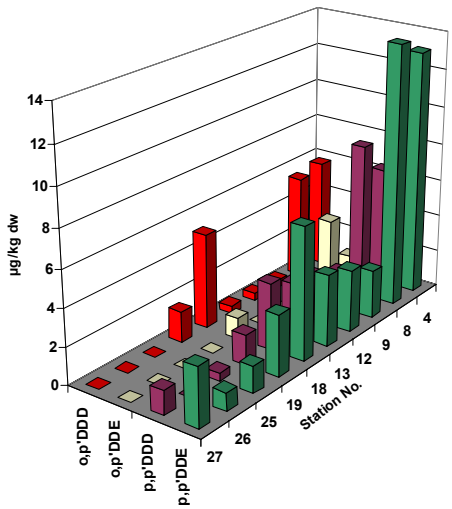


Figure 27: DDT metabolites in mussel tissues of Abu Qir Bay. Stations 4 to 19 represent *Mactra corallina* and from 25 to 27 represent *Tapes decussata*.

Only γ-, α- and δ- isomers of HCHs were observed in the mussel tissues of *Mactra corallina* (**Figure 28**). Like in sediments, γ- and α- isomers were the most abundant isomers being detected in 4 samples (4, 8, 18, and 19) of *Mactra corallina* with higher concentrations of γ-isomer compared to the α-isomer. Concentrations of HCHs ranged from <DL to 10.9 µg/kg dw (**Appendix I, Table A31)**.

Dieldrin was detected in 4 samples of *Mactra corallina* (stations 4, 8, 12, 13) with concentrations ranging from <DL to 11.5µg/kg dw. Concentration detected in station 4 in front of the Maadeya Outlet was much higher than concentrations detected in the three other samples which were close to each other (**Appendix I, Table A31**).

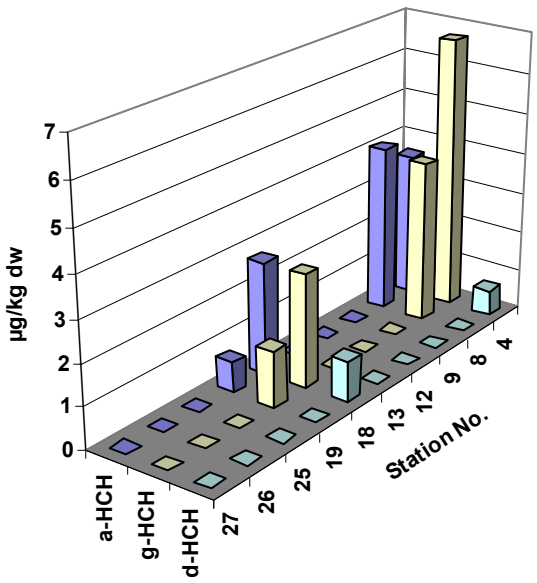


Figure 28: Distribution of HCH isomers in mussel tissues of Abu Qir Bay. Samples from 4 to 19 represent *Mactra corallina* and from 25 to 27 represent *Tapes decussata*.

All the other investigated pesticides (Heptachlor and its epoxides, methoxychlor, PCBz, HCBz and mirex) were either detected in low concentrations compared to the rest of the investigated pesticides or found below the limit of detection (**Appendix I, Table A31**).

The distribution of pesticides in both species reveals that tissues of *Mactra corallina* are more contaminated with pesticides compared to *Tapes decussata*. At the same time, samples of *Mactra corallina*, which are influenced by effluents, discharged from Lake Edku (stations 4, 8) and Abu Qir Drain (stations 18, 19) showed higher degree of contamination similar to what was detected in the bay sediments. Thus it can be concluded that concentrations of pesticides detected in tissues of mussels are influenced by sampling locations. Significant positive correlation was observed between lipid % in *Mactra corallina* and some of the investigated organochlorine pesticides (HCHs: r = 0.81; chlordanes: r = 0.77; endosulfane: r = 0.74; heptachlor: r = 0.69; DDTs: r = 0.65).

Significant positive correlations were also observed between concentrations of some organochlorine pesticides in sediments and tissues of *Mactra corallina* (endosulfane: r = 0.97; methoxychlor: r = 0.92; chlordanes: r = 0.90; γ-HCH: r = 0.80).

3.7.1. Comparison between concentrations of chlorinated organic compounds in mussel tissues of Abu Qir Bay with concentrations worldwide

Concentrations of the chlorinated organic compounds in the tissues of the two species investigated in the present study were compared with concentrations in different species worldwide and in the previous studies performed along the Egyptian Coast. As shown in **Appendix I, Table A32**, detected concentrations in the present study were generally lower than most of the concentrations recorded in other species worldwide. At the same time, concentrations were generally much lower than concentrations recorded in fish tissues and mussel samples investigated previously in Abu Qir Bay or in other parts along the Egyptian Coast (**Figure 29**) but this can be compared only as a magnitude due to the difference either in the species, sampling locations and/or difference in the sampling period which could have a great influence on the obtained concentrations. No trend can be observed for almost all the investigated chlorinated organic pollutants because of the data gaps which appeared when literature was collected for the last two decades. In addition, most of the previous studies concentrated on different fish species. At the same time, none of the two mussel species sampled in the present study were investigated previously in Egypt.

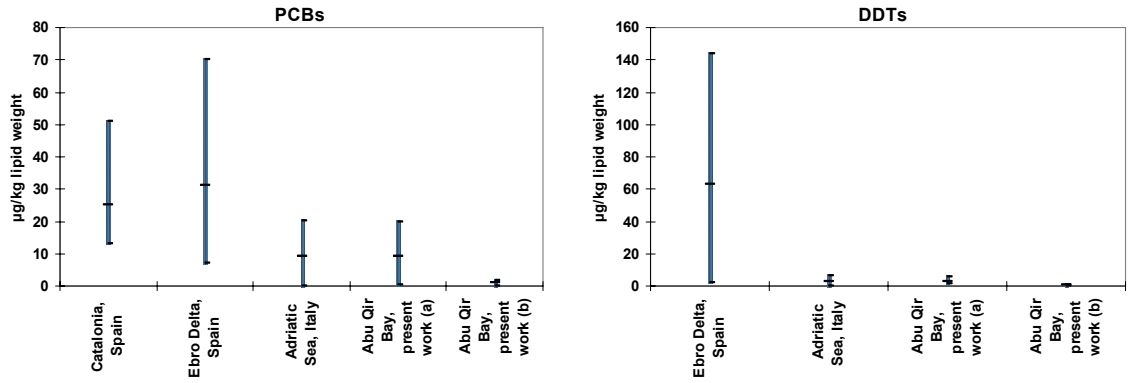


Figure 29: Ranges and average concentrations of PCBs and DDTs (µg/kg lipid weight) in mussel species worldwide compared to the present work. (*Mytilus galloprovincialis* in Spain; (a): *Mactra corallina*, (b): *Tapes decussata*).

3.8. PAHs in sediment and mussels of Abu Qir Bay

3.8.1. Spatial distribution

Concentrations of PAHs (**Appendix I, Table A33**) ranged from <DL to 2660 µg/kg dw in surfacial sediments of Abu Qir Bay with an average concentration of 478 µg/kg dw. The maximum detected concentration was observed in station 27 in the western part of the bay, where the location is affected by the intensive shipping activities. Contamination with PAHs in the sediments was observed all over the bay (**Figure 30**) with higher concentrations recorded in the nearshore stations especially in front of the Fertilizer Company (station 2: 897 µg/kg dw and station 20: 825 µg/kg dw), Abu Qir Drain (station

1: 572 µg/kg dw), in front of the Maadeya Outlet (station 4: 766 µg/kg dw) and in front of the Electric Power Plant (station 3: 600 µg/kg dw). Concentrations generally decrease in the seaward direction except for station 14, which shows an elevated concentration of PAHs (930 µg/kg dw). This observation was substantiated by other studies, where PAHs concentrations were higher in areas adjacent to discharged effluents rather than other areas (Barrick and Prahl, 1987; Sanders, 1995; Daskalakis and O'Connor, 1995). Based on the average calculated concentrations for each individual PAH, the following descending order can be observed: Fla > Pyr > Nap > Phn > Flr > BaA > Ace > Chy > Ant > BaP > BbF > BkF > Acy > InP > DibA > BghiP. PAHs with mass 202 (Fla and Pyr) and 252 (BbF, BkF and BaP) predominated in the molecular mass profiles for samples from the Abu Qir Bay (**Figure 31**). Mass 202 represents from 11.4 % to 55.0 % of the total PAH concentrations with an average value of 21.7 %. Mass 252 came in the second order representing from 3.53 % to 38.9 % of the total PAH concentrations with an average value of 16.3 %.

The predominance of mass 202 in most cases may indicate significant anthropogenic inputs (Hites et al. 1980; Bates et al. 1984; Lipiatou and Saliot, 1991). In stations 1 and 21, mass 202 predominate the molecular mass profile followed by mass 178 (**Figure 31**). Both stations are located in front of Abu Qir Drain and thus they appear to be influenced by the wastewater discharged from the drain possibly containing the lower molecular weight PAHs (mass 178). On the other hand, stations 9, 12 and 13 were predominated by mass 252 followed by mass 178 (**Figure 31**). This could possibly be related to the location of these stations either in front of or close to the Wepco Petroleum Company.

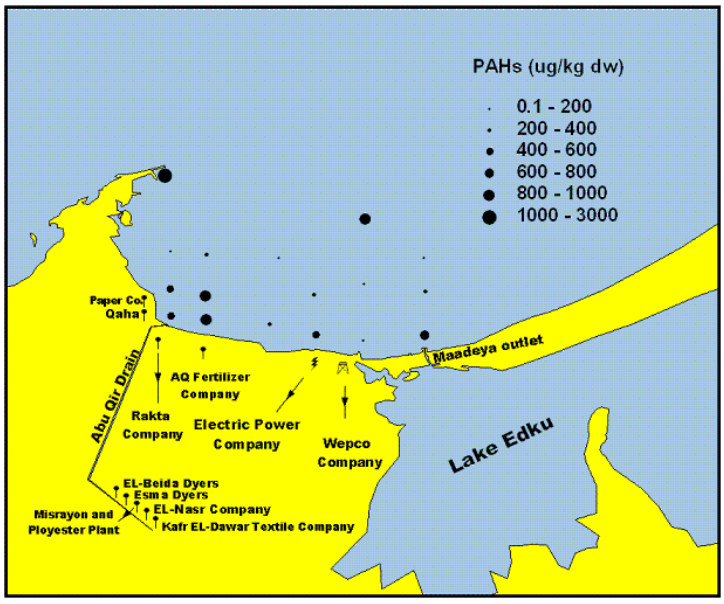


Figure 30: Spatial distribution of PAHs (µg/kg dw) in surfacial sediments of Abu Qir Bay.

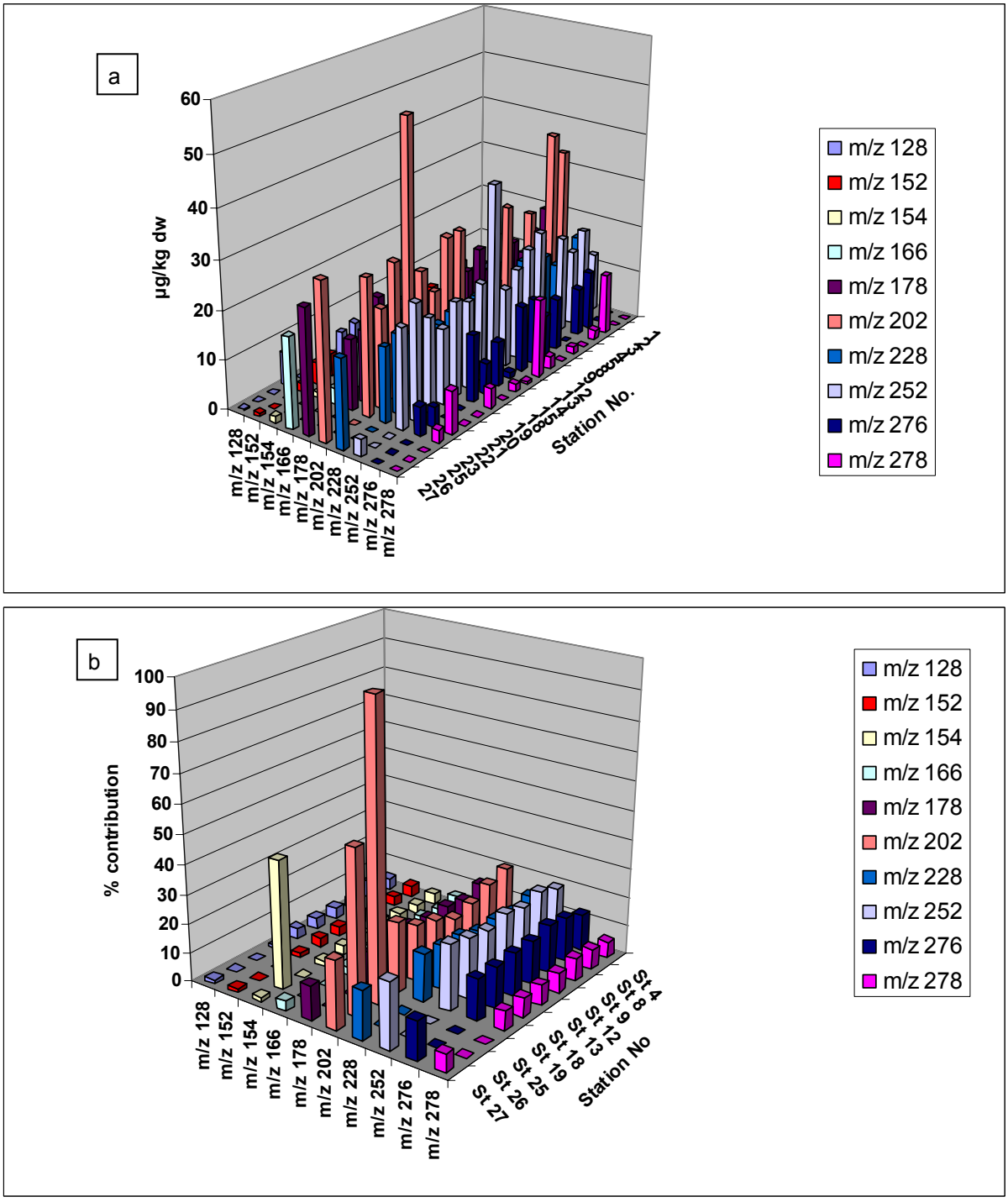


Figure 31: Percent contribution of the molecular mass profile of PAHs in surfacial sediments (a) and mussel samples (b) of Abu Qir Bay.

PAHs generally occur as complex mixtures and not as single compounds. High temperature combustion processes emit the high molecular weight PAHs (HMW), which are represented by PAHs with 4 or more rings (Neff, 1979). Concentrations of 4 to 6 rings PAHs typical for combustion (Barrick and Prahl, 1987; McCready et al. 2000; Vane et al. 2007) (Fla + Pyr + BaA + Chy + BbF + BkF + BaP + InP + DibA + BghiP) ranged from 32.5 µg/kg dw to 1393 µg/kg dw with an average concentration of

286 µg/kg dw (**Appendix I, Table A34**). These concentrations represented from 47.0 % to 78.2 % of the total PAH concentrations with an average value of 51.6 %.

Some PAHs such as BaA, BbF, BkF, BaP, Chy, DibA and InP have a mutagenic and genotoxic potential (Arcos and Argus, 1975; WHO, 1989). The concentrations of these PAHs (ΣPAH_{tox}) ranged from 25.6 µg/kg dw to 576 µg/kg dw with an average concentration of 164 µg/kg dw (**Appendix I, Table A34**). These concentrations represented an average of 33.7 % of the total PAH concentrations and range from 21.6 % to 55.2 %.

There have been a number of studies which measured PAHs adjacent to urban areas (e.g. Pruell and Quinn, 1985; Barrick and Prahl, 1987; O'Connor, 1991; Kennicutt et al. 1994). In many cases, the number of PAHs summed to obtain the total PAHs was different and the concentrations of PAHs in sediments were extremely variable.

The processes controlling levels of PAHs in sediment samples are complex. Bulk sediment properties such as TOM and grain size, have been shown to account partly for PAHs variability in sediments (Barrick and Prahl, 1987; Kennicutt et al. 1994). Several authors have observed that PAHs in sediments are mainly associated with the organic matter (Neff, 1979; Prahl and Carpenter, 1983; Knezovich et al. 1987; Evans et al. 1990; Al-Ghadban et al. 1994), and PAHs sediment content depends on grain size distribution (Law and Andrulewicz, 1983; Readman et al. 1984; Raoux and Garrigues, 1993; Velinsky et al. 1994; De Mora et al. 2004). Law (1981) stated that finer particles have a higher adsorptive capacity for organic substances owing to their greater effective surface area. However, concentrations of total PAHs (ΣPAHs) in sediments of Abu Qir Bay showed weak correlation with TOC (r = 0.18) and clay (r = 0.14) contents. This agrees with Simpson et al. (1998), who showed that the relationship between total PAHs and organic carbon was only significant for highly contaminated sites where total PAH concentrations were greater than 2000 µg/kg dw. In the present study, except for station 27, all the investigated sediment samples had total PAH concentrations lower than 2000 µg/kg dw. It was also found that sediments that contain soot particles, which are formed from combustion of coal, refined fossil fuels (diesel and fuel oils) and vegetation (biomass burning), can bind or occlude PAHs, thus making them less available to partition with TOC in sediments (Maruya et al. 1996; Gustafson et al. 1997). Lack of significant correlation suggests also the introduction of fresh loadings of PAHs. Katsoyiannis (2006) reported that in an environment where there is continuous introduction of fresh contamination, lack of correlation should be expected, at least until equilibrium is reached.

Relatively high concentrations of low molecular weight PAHs (2 and 3 rings) recorded in the sediments of Abu Qir Bay might be an evidence of recent pollution and thus supports the absence of correlation between PAH concentrations and TOC content.

Concentrations of PAHs in the mussel samples are shown in **Appendix I, Table A35**. High concentrations of PAHs were generally observed in both species. PAHs concentrations ranged from 11.4 µg/kg dw (station 25) to 3875 µg/kg dw (station 27) with an average concentration of 1303 µg/kg dw in *Tapes decussata* and 242 µg/kg dw to 2827 µg/kg dw with an average concentration of 1070 µg/kg in *Mactra corallina*. In contrast to all the investigated pollutants, the highest detected concentration of PAHs was observed in *Tapes decussata* (station 27) in the western part of the bay like in the sediments. High PAH concentrations were also observed in stations 4, 8, 18 and 19. Concentrations of PAHs in the mussel samples followed the sediment concentrations. High significant positive correlation was found between the total PAH concentrations in the sediments and the mussels in the bay (r = 0.90). At the same time, high degree of correlation was found between PAHs concentrations and lipid content in both species (r = 0.91 in *Mactra corallina* and r = 0.97 in *Tapes decussata*). Concentrations of PAHs in offshore and in the western part of the bay (stations 25, 26) were lower than the nearshore mussel samples (**Appendix I, Table A35**). In station 25, only Fla was detected and in station 26, Fla and Ace

The full range of PAHs (2-6 rings) was detected in the mussel tissues. The mussels contained mainly tetra-aromatic isomers (Fla, Pyr, BaA and Chy), penta-aromatic isomers (BbF, BkF, BaP and DibA) and hexa-aromatics (InP and BghiP) rather than di and tri-aromatics (Nap, Flr, Phn and Ant). Like in sediments, PAHs in the mussel tissues were dominated by the higher molecular weight PAHs (4-6 rings), which represented an average value of 67.4 % of the total detected PAH isomers (56.0 %-100 %). Several studies have shown that bivalves preferentially bioaccumulate 4-, 5- and 6-ringed PAHs rather than 2- and 3-ringed PAHs (Porte and Albaiges, 1993; Hickey et al.1995; Baumard et al.1998a). In addition, laboratory assays pointed out that bivalve preferably bioaccumulate heavier PAHs following increase in K_{ow} (octanol-water partition coefficient; Neff, 2002). Lower molecular weight PAHs are more soluble in water than heavier PAHs (Djomo et al.1996; Porte and Albaiges, 1993) and, therefore the latter appear associated with particles while the former are preferentially dissolved. Mussels are filter-feeding bivalves and are exposed to both dissolved and particle bound PAHs present in the water column. The more hydrophilic 2- and 3-ring PAHs, dissolved in the water column, will be readily available to mussels. Mussels are also exposed to the heavier molecular weight PAHs (four or more rings) associated with particulate matter. Although these ultimately gravitate to the sea-bed, sediment particles are regularly re-suspended as a result of winter storms, or as a consequence of tidal streams and wave action. In waters of high turbidity, where particles are re-suspended regularly, filter-feeding bivalves will contain a higher proportion of the more hydrophobic 4- to 6-ring compounds due to accumulation of PAHs from the sediment. The higher molecular weight PAHs can accumulate in biota if the uptake route is via the food or sediment especially when the molluscs live in contact with sediments. The bioavailability of PAHs will be affected by the organic carbon content and particle size of the sediment. In Abu Qir Bay, sediments were characterized by low TOC content and the dominance of the sand fraction, which could result in greater chance of PAH uptake by the mussels. Similar to sediments, PAHs with mass 202 and 252 predominate in the molecular mass profiles for mussel samples in the bay (**Figure 31**). Mass 202 represented an average value of 31.0 %

of the total detected PAHs in the mussel tissues ranging from 14.0 % to 100 %. Mass 252 came in the second order followed by mass 276.

3.8.2. Comparison between PAH patterns in sediments and mussel samples of Abu Qir Bay

A comparison of the PAH pattern in sediments and mussels is shown in **Figure 32**. Similar pattern can be observed between sediments and mussels of stations 4, 8 and 19, all representing *Mactra corallina*. Significant positive correlation was observed between PAH concentrations in sediments and mussels at these three locations (r = 0.93, 0.81 and 0.86 respectively). The three locations had sediment PAH concentrations higher than 200 µg/kg dw. On the other hand, all the sediment samples with PAH concentrations lower than 200 µg/kg dw showed poor correlation with mussel PAH concentrations. Looking at **Figure 32** one can deduce the difference in the pattern of PAH isomers distribution in stations 9, 12, 13 and 18 between sediments and mussels which was characterized by a marked increase in higher molecular weight PAHs in the mussel tissues. Thus, it can be concluded that the mussels are not only affected by the bioavailable fraction of PAHs in sediments, but possibly also by PAHs distributed in the water column either in soluble form or in the particulate form which in addition to exposure to contaminated food could be more important than the soluble form due to the dominance of the high molecular weight PAHs in the mussel tissues.

In station 27, where the maximum detected concentration of PAH in sediments and mussel tissues can be observed, sediments were characterized by the dominance of Flr, Phn, Fla, Pyr and Chy, which represent the 3, 4 and 5 rings PAHs. The other high molecular weight PAHs (5, 6 rings) were either not detected or found at very low concentrations (**Figure 32**). But in the mussel tissues corresponding to this location, dominance of the higher molecular weight PAHs can be observed. In most of the investigated samples of both species, lower molecular weight PAHs were in most cases much lower than the higher molecular weight PAHs, which could possibly be related to a metabolic pathway where the mussels can metabolize the low molecular weight PAHs.

3.8.3. Origin of PAHs in Abu Qir Bay

The concentrations and types of PAHs found in sediments have been shown to reflect source characteristics (Latimer et al. 1990; Ngabe, 1992; Singh et al. 1993) and be related to the physico-chemical properties of individual PAHs that influence sediment binding capacity. PAH in urban areas, such as Abu Qir Bay, can originate from a variety of sources such as combustion of fossil fuels (e.g., cooking and heating oils, coal burning, vehicle emissions) and biomass burning (e.g., fireplaces, controlled burning) (Simoneit, 1985). These are classified as PAHs of pyrogenic origin. Combustion-derived PAH in the atmosphere can enter the water column directly by gaseous exchange across the air–water interface, dry deposition of airborne particulate matter, or wet deposition by rainfall, and indirectly by urban runoff (e.g., street surfaces, storm water discharge) (Hoffman et al. 1984; Dickhut and Gustafson, 1995; Dickhut et al. 2000; Tsai et al. 2002).

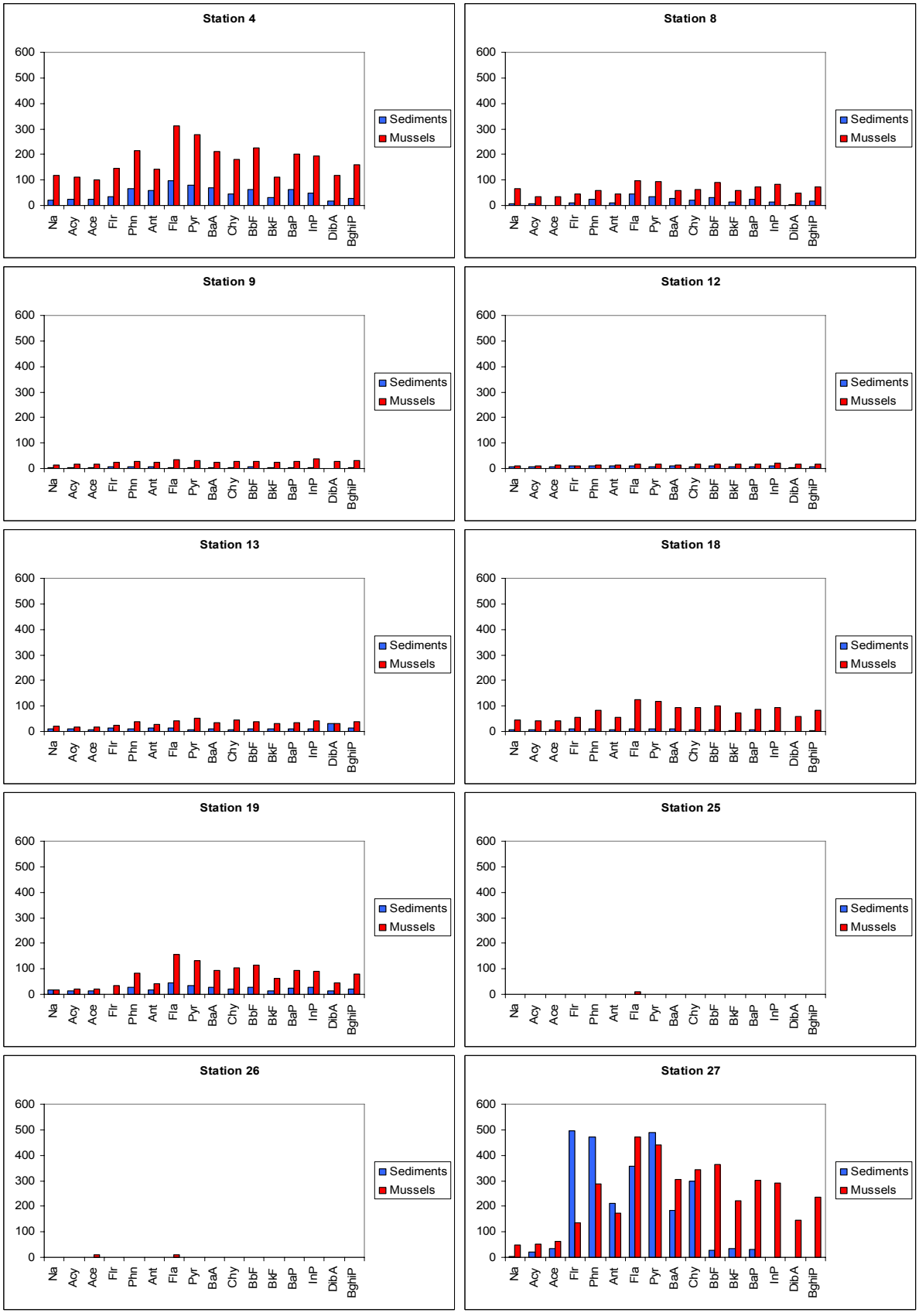


Figure 32: Comparison of PAH patterns of sediments and mussels of Abu Qir Bay.

Unburned fossil fuels (crude oil and its refined products formed by slow maturation of organic materials under the geochemical gradient conditions of temperature and pressure referred to as petrogenic PAHs) can also impart their PAH signature to the marine environment (Hites et al. 1980; Simcik et al. 1996; Countway et al. 2003), primarily by street surface runoff and accidental spills. In addition, PAHs can be formed from the short-term diagenetic degradation of biogenic precursors (diagenetic PAHs) (McElory et al. 1989; Oros et al. 2007).

PAH isomer pairs have similar physicochemical properties and similar dilution and distribution with particulate matter and other environmental phases (Dickhut et al. 2000), thus ratios of PAH isomer pairs can be applied as distinct chemical tracers to infer possible PAH sources in environmental samples. For instance, PAH isomer pair ratios were used to identify automobile emissions as the major source of PAH in the Chesapeake Bay (Dickhut et al. 2000). Also, Yunker et al. (2002) applied PAH isomer pair ratios to show that PAH in the Fraser River Basin and Estuary (British Columbia, Canada) were derived from biomass, coal, and petroleum combustion.

The use of PAH ratios for source assignments in sediments requires an understanding of the relative discrimination ability (relative thermodynamic stability) of different parent PAHs, the characteristics of different PAH sources and the changes in PAH composition between source and sediment (the relative stability of different PAH isomers and PAHs from different sources) (Yunker et al. 2002). In order to minimize confounding factors such as differences in volatility, water solubility and adsorption, ratios calculations are usually restricted to PAHs within a given molecular mass (Readman et al. 1987; Mcveety and Hites, 1988). For parent PAHs, combustion and/or anthropogenic input is often inferred from an increase in the proportion of the less stable `kinetic´ PAH homologous relative to the more stable `thermodynamic` ones (Yunker and Macdonald, 1995) and the stability of the lighter PAH homologous has been calculated to support such interpretations (Budzinski et al. 1997; Yunker et al. 2002). It was found that the PAH homologous with the masses 202 and 276 isomers have the greatest range in stability and hence good promise as indicators of petrogenic vs. pyrogenic sources, whereas PAHs with masses 278 and 228 showed little promise as such indicators.

PAHs of molecular mass 178 and 202 are commonly used to distinguish between pyrogenic and petrogenic sources (Gschwend and Hites, 1981; Sicre et al. 1987; Budzinski et al. 1997; Soclo et al. 2000). Ratio values such as Phn/Ant (m = 178) and Fla/Pyr (m = 202) had been used by previous workers (Sicre et al. 1987; Budzinski et al. 1997; Baumard et al. 1998a; Soclo et al. 2000). Petroleum often contains more phenanthrene relative to anthracene, which is a more thermodynamically stable tricyclic aromatic isomer, so that the Phn/Ant ratio is observed to be very high in the case of petrogenic pollution with PAHs but low in pyrolytic contamination cases (Gschwend and Hites, 1981; Soclo et al. 2000; Yang, 2000). Budzinski et al. (1997) found that sediments with Phn/Ant > 10 were mainly contaminated by petrogenic inputs and Phn/Ant < 10 was typical of pyrolytic sources. In addition to the Phn/Ant ratio, Fla/Pyr ratio also indicated the origin of PAHs. Sicre et al. (1987) found that a Fla/Pyr < 1 was attributed to petrogenic sources and values greater than 1 were obviously related to a pyrolytic

origin. Combustion of coal and wood gave Fla/Pyr ratios of 1.4 and 1, respectively, while crude oil and fuel oil had values of 0.6-0.9 (Gschwend and Hites, 1981). Moreover, pyrene can predominate over fluoranthene in atmospheric urban aerosols (Fla/Pyr between "0.6 to 0.8") (Muel and Saguem, 1985; Benner et al. 1989). In order to estimate PAHs sources, the Phn/Ant ratios were plotted against Fla/Pyr according to Budzinski et al. (1997). It was found that 80 % of the investigated sediment samples have pyrogenic origin of PAHs (**Figure 33a**). At the same time, only 4 samples (stations 9, 18, 20 and 27) showed a mixed pattern of contamination (petrogenic and pyrogenic). For the mussel samples (**Figure 33b**), the pyrolitic origin was the dominant source in most of the investigated samples with 2 samples of *Mactra corallina* (stations 12 and 13) showing a mixed pattern of contamination.

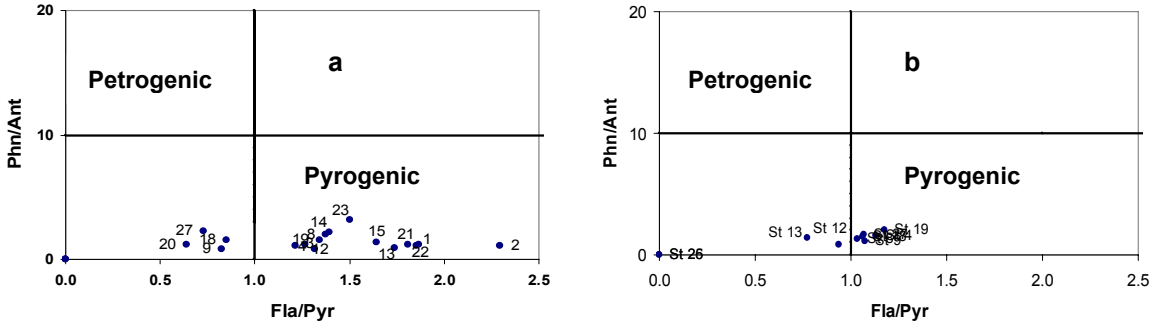


Figure 33: Phn/Ant versus Fla/pyr plots of PAHs in sediments (a) and mussels (b) of Abu Qir Bay.

Another four molecular ratios were used in the present study: Ant/Ant+Phn, Fla/Fla+Pyr, BaA/BaA+Chy and InP/InP+BghiP (**Figure 34**). An Ant to Ant + Phn ratio < 0.1 usually is taken as an indication of petroleum while a ratio > 0.1 indicates a dominance of combustion (Budzinski et al. 1997). A Fla to Fla + Pyr ratio of 0.5 is usually defined as the petroleum/combustion transition point (Budzinski et al. 1997), but in practice this boundary appears to be less definitive than 0.1 for Ant/178. The Fla/Fla+Pyr ratio is below 0.4 for most petroleum samples, between 0.4 and 0.5 for of liquid fossil fuel (vehicle and crude oil) combustion and above 0.5 in kerosene, grass, most coal and wood combustion

The higher mass PAHs usually are minor contributors to refined petroleum products (Williams et al. 1986; Wang et al. 1999) and generally are present in significant amounts only in higher fractions such as asphalt (Wakeham et al. 1980; Readman et al. 1987) and possibly in bitumen or coal (Yunker et al. 2002). Because very low proportions of BaA and InP are rarely observed in combustion samples, a BaA/BaA+Chy or InP/InP+BghiP less than 0.2 likely indicates petroleum, a ratio value of BaA/BaA+Chy between 0.2 and 0.35 indicates petroleum combustion, and a value higher than 0.35 is an indicative of combustion source (Yunker et al. 2002).

Few source specific interpretations have been provided for the InP/InP+BghiP ratio (Sicre et al. 1987; Gogou et al. 1996).

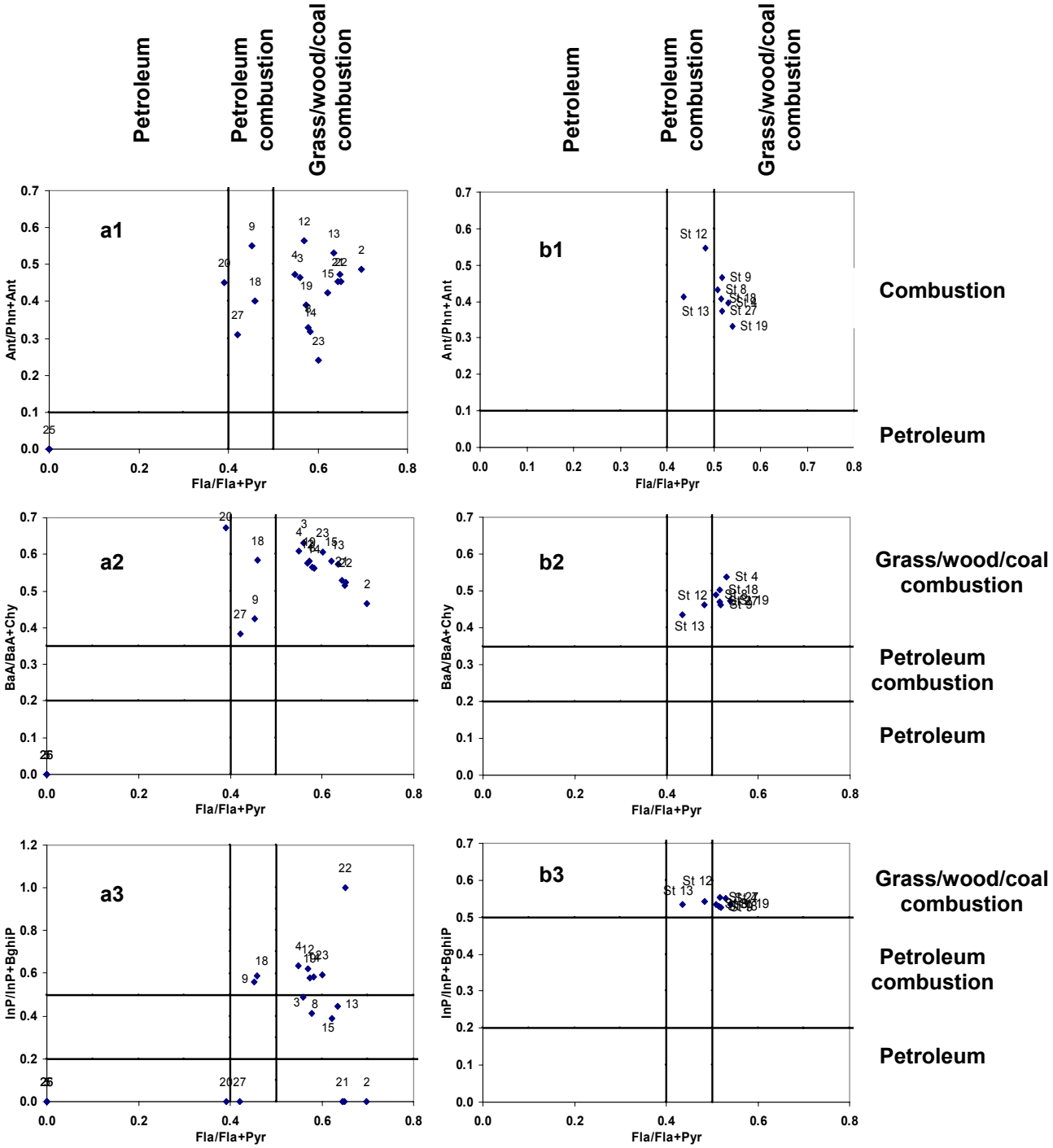


Figure 34: Molecular ratios applied for PAHs in sediments (a) and mussel samples (b) of Abu Qir Bay.

Literature values are above 0.5 for grass combustion, wood soot, creosote and almost all wood and coal combustion aerosols and a bush fire but are below 0.5 for all savanna fire (Yunker et al. 2002). In contrast, combustion products of gasoline, kerosene, diesel and crude oil all have ratios below 0.5 with vehicle emissions falling between 0.24 and 0.4. Accordingly, InP/InP+BghiP ratios < 0.2 likely imply

petroleum, between 0.2 and 0.5 liquid fossil fuel (vehicle and crude oil) combustion and the ratios > 0.5 imply grass, wood and coal combustion.

Calculated molecular ratios are shown in **Appendix I, Tables A34** and **A36** for sediments and mussel samples respectively. Molecular ratios (Ant/Ant+Phn, BaA/BaA+Chy and InP/InP+BghiP) are plotted against Fla/Fla+Pyr in **Figure 34a** and **b**. It can be observed from the calculated ratios that the dominant source of PAHs in sediments of Abu Qir Bay is the combustion process, either petroleum combustion (less frequent) or wood, coal and grass combustion (more frequent). At the same time, only station 20 (in front of the Fertilizer Company) shows a mixed pattern or petroleum and combustion sources. Petroleum combustion fingerprints are greatly emphasized in station 27 (in the western part of the bay), which could possibly be related to the shipping activity. At the same time, calculated values of InP/InP+BghiP indicate that PAHs in sediments from stations 13, 8, 15 and 3 showed a petroleum combustion fingerprint which could possibly be related to the occurrence of the Wepco Petroleum Company. Applying the different molecular indices to PAHs recorded in the mussel tissues, it can be observed that the Pyrogenic origin dominates in all the investigated mussels in the bay (**Figure 34b**).

Based on the obtained concentrations of PAHs in the bay sediments and the calculated molecular ratios, one can conclude that the combustion activity is the major cause of PAHs occurrence in the bay sediments both by direct atmospheric deposition and with the water discharged from the Abu Qir Drain and the Maadeya Outlet, where high concentrations of PAHs were observed in samples affected by these two wastewater discharges. At the same time, it appears that the shipping activity is responsible for the major contamination in the bay sediments, where the maximum detected PAH concentration is located in Abu Qir Harbour in the western part of the bay possibly due to the shipping exhaust systems and the shipping repairing activities.

3.8.4. Comparison between concentrations of PAHs in sediments and mussels of Abu Qir Bay with concentrations worldwide

Concentrations of PAHs recorded in surfacial sediments of Abu Qir Bay were compared with sediment concentrations worldwide (**Appendix I, Table A37**). It was clear that lower PAHs concentrations were observed in Abu Qir Bay sediments compared to most of the coastal sediments in France, Spain, USA and other parts of the world (**Figure 35** and **Table A37**). At the same time, much higher concentrations of PAHs were observed along Alexandria Coast in EL-Mex Bay and in the Western Harbour. Close concentrations of PAHs were observed in the present study when compared with concentrations obtained by EL-Deeb et al. (2007), although slightly higher concentrations were observed in the present study. Similar to his study, the maximum detected concentration was found in the western part of the Bay. Differences in the sampling locations may have caused a change in the degree of similarity between his study and the present study.

On the other hand, concentrations recorded in the two mussel species investigated in the present study were higher than most of the concentrations recorded in mussels of the Mediterranean Sea and other parts worldwide (**Figure 35** and **Appendix I, Table A38**), although different species were investigated. This could be related either to the occurrence of PAHs in Abu Qir Bay sediments in a more bioavailable form, species difference, sampling periods variability and/or the better accumulation capacity of both species. Comparing the obtained PAHs concentrations with previous studies, one can realize that much lower concentrations were obtained in the present study compared to all the investigated species in Abu Qir Bay and the Red Sea.

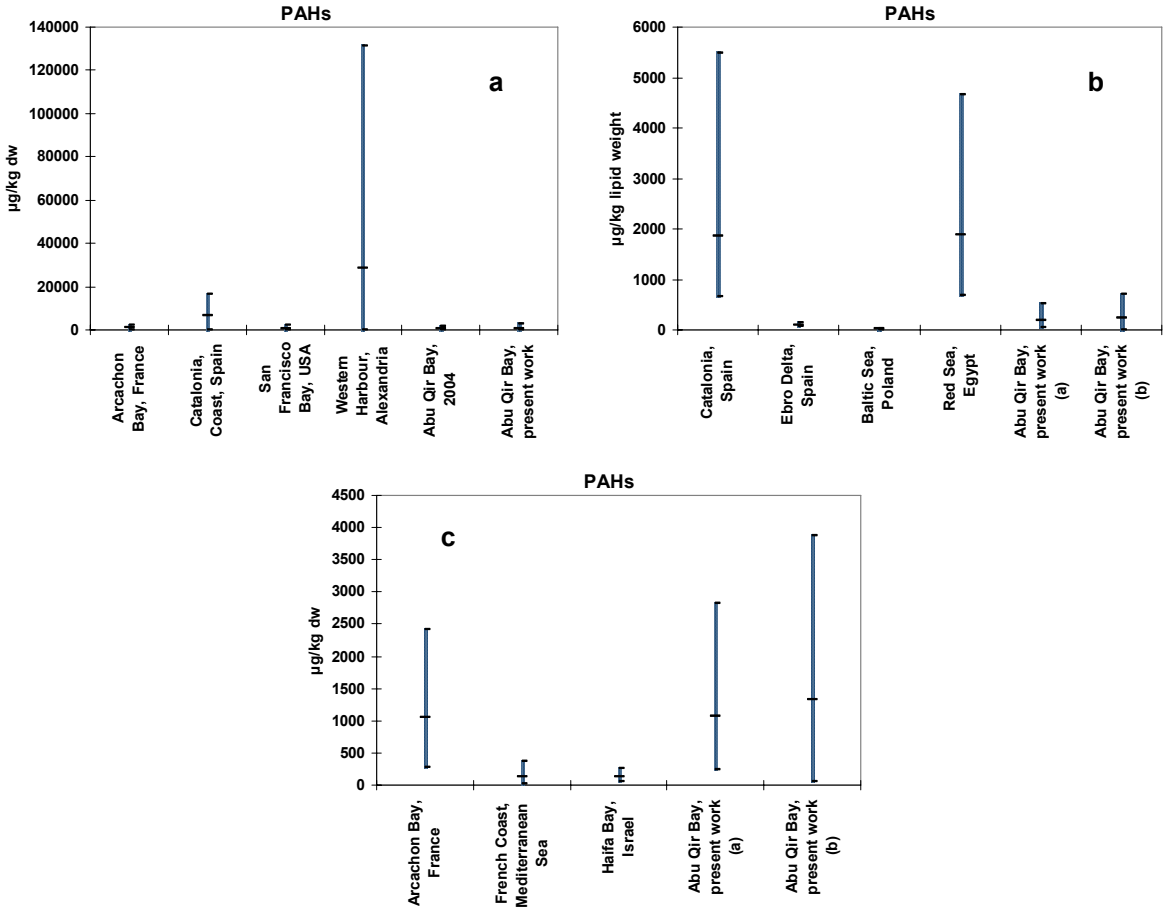


Figure 35. Ranges and average concentrations of PAHs (µg/kg) in surfacial sediments (a) and mussel species (b and c) worldwide, and along the Egyptian Coast compared to the present work. (*Mytilus galloprovincialis* in Catalonia and Ebro Delta, Spain and Adriatic Sea, Italy, the French Coast and Arcachon Bay, France; *Mactra corallina* in Haifa Bay. *Mytilus edulis* in the Baltic Sea, Poland; *Brachiodonates sp.* in the Red Sea, Egypt; a: *Mactra corallina*; b: *Tapes decussata*.

4. Risk assessment

The risk assessment performed in the present study included both the ecological risk assessment (ERA) for evaluating the environmental quality of Abu Qir Bay by investigating the bay sediments and mussel species as bioindicators, and the human health risk assessment (HHRA), where the possibility of occurrence of adverse health effects from the ingestion of the mussel species was examined.

4.1. Ecological risk assessment (ERA)

The basic approach used to derive the risk assessment in Abu Qir Bay was shown in the introduction (section 1.7) and **Figures 1** and **2**. The proceeding sections will discuss in details the formulation of the ERA in Abu Qir Bay.

4.1.1. Problem formulation

Problem formulation includes ecosystem characterization, contaminants of interest, pathway analysis, assessment endpoint development, and measurement endpoint identification. Problem formulation results in the development of a problem statement that is addressed in the analytical step. All these points investigated in the problem formulation become finally represented in the site conceptual model identifying appropriate standards and criteria to assess the data collected.

A full description of Abu Qir Bay is given in chapter 1 (Section 1.8). Organic and inorganic pollutants were selected for investigation in the present study. Organochlorine pesticides, PCBs, PAHs and heavy metals were included. (See chapter 2). Based on the literature survey, the selected organochlorine pesticides for investigation in the present study were either applied in Egypt or detected in coastal sediments.

Assessment endpoints are explicit expressions of actual environmental values of commercial or social values that are to be protected. Three principle criteria are used to select ecological values that may be appropriate for assessment endpoints: 1) ecological relevance, 2) susceptibility to known or potential stressors, and 3) relevance to management goals (USEPA, 1998). Assessment endpoints may include organism populations or communities (e.g., fish) or nonbiological characteristics (e.g., water or sediment quality). Populations may be deemed at risk if reproduction or survival of individuals is determined to be significantly impacted. Water and sediment quality are considered to pose a risk to invertebrates if chemical levels exceed acceptable benchmark values. This kind of risk assessment will determine assessment endpoints based on the likelihood that an adverse effect will occur.

Selected assessment and measurement endpoints in the present study are given in **Table 17**. Appropriate selection and definition of assessment endpoints are critical to the utility of risk assessment, as the endpoints focus the risk assessment design and analysis. It is neither practical nor possible to directly evaluate risks to all of the individual components of the ecosystem at the site.

Table 17: Assessment and measurement endpoints for the SLERA of Abu Qir Bay.

Receptor	Assessment endpoint	Receptor type	Measurement endpoint
Sediments	Sediment quality	Abiotic	- Sediment concentrations (site) - Sediment quality guidelines for protection of aquatic life (collected from literature)
Bivalves	Species functioning	Biotic	- Tissue concentrations (site) - Receptor toxicity data (collected from literature)

In the present study, the assessment will consist on the recognition of possible generic adverse effects of the investigated chemicals towards the marine ecosystem, and particularly the benthic community, which is to be the most susceptible to the sediment bound contaminants (Jones et al. 1999). Benthic invertebrate communities are heterogeneous assemblage of organisms that inhabit bottom substrates. Benthic invertebrates are susceptible to contaminant exposure because they live and feed directly in the sediment, where most contaminants are concentrated. Benthic invertebrates play several important roles in the aquatic community, including the mineralization and recycling of organic matter. Like aquatic invertebrates, benthic invertebrates constitute a vast portion of the basis of the food chain for aquatic ecosystems and are, therefore, important in energy transfer. In doing so, benthic invertebrates play an integral role in nutrient and energy cycling, supporting the productivity of the entire ecosystem. Benthic invertebrates are important trophic links in aquatic communities because they consume bacteria, plankton, and detritus, and are a dominant prey base for certain species of fish, birds and other benthic organisms. Upper trophic levels can be affected not only by reduced prey abundance, but also by trophic transfer of accumulated contaminants in benthic invertebrates.

Several ecological aquatic receptors are located in Abu Qir Bay including fish species and benthic fauna. According to Fishar and EL-Haweet, (2005), the pollution problem in the bay has caused both the change and loss of the habitat of marine fauna and change in the water quality of the bay. The study performed by Fishar and EL-Haweet, (2005) revealed that 51 fish species were recorded in Abu Qir Bay (43 marine species, 6 catadromous species and 2 freshwater species) and 9 crustacean species. In addition, 29 different species of the macrobenthic community were recorded, with arthropods representing 48 % of the total detected species, molluscs representing 36.5 % and annelids representing 15.4 % (Fishar and EL-Haweet, 2005). This survey was performed in the period from 2003 to 2004 and when they compared their results with previous studies, they concluded that there was a remarkable decrease in the biodiversity of fishes and benthic fauna as a result of the intensive human impacts.

Measurement endpoints are quantifiable ecological characteristics that are related to the valued characteristic chosen as the assessment endpoint (USEPA, 1992). The measurement endpoint should represent the same exposure pathway, and mechanism of toxicity, as the assessment endpoint it represents. In the present study, measurement endpoints depended on measuring the chemical concentrations of the target pollutants in the sediments and the mussel tissues.

For toxicity to occur, a contaminant must be present, a receptor must be present, and there must be a complete exposure pathway by which the receptor is exposed to the contaminant. The conceptual site model identifies where contaminant interactions with biota can occur. A conceptual model describes the fate and transport of site contaminants through the physical system (sediments of Abu Qir Bay) and key receptor exposure pathways. The conceptual site model used in the SLERA of Abu Qir Bay is presented in **Figure 36**. As shown in **Figure 36**, the selected exposure media was the bay sediments. The ecological receptors included in this risk assessment were the benthic organisms, although they were not investigated directly. The selected exposure route was the direct contact of the benthic organisms with the bay sediments.

4.1.2. Exposure characterization

This section describes how the exposure of ecological receptors to chemicals in various environmental matrices (i.e., sediment, tissue) was quantified. It begins with a description of the environmental concentrations used, followed by a description of the approach used for quantifying exposure to each receptor.

Chemical concentrations

Chemical concentrations of trace elements and trace organic pollutants in sediments and the mussel samples of Abu Qir Bay are given and discussed in chapter 3 (results and discussion). A summary of the chemical data evaluated are listed in **Table 18**. Only contaminants with available guidelines were evaluated in the SLERA. For contaminant concentrations in sediments, the maximum concentration for each pollutant was used in the SLERA as a conservative assumption. For *Mactra corallina*, the upper 95 % confidence level (95 % UCL) was selected, which provides a more conservative estimate of the true mean. Because of the uncertainty associated with estimating the true average concentration of a site (because of the limited sampling sites), the 95 % UCL provided a reasonable confidence that the true site average will not be underestimated (Conservatism). In the case of *Tapes decussata*, the number of samples investigated (n = 3) was not enough to calculate the 95 % UCL and for this reason, the maximum concentration of each pollutant was used.

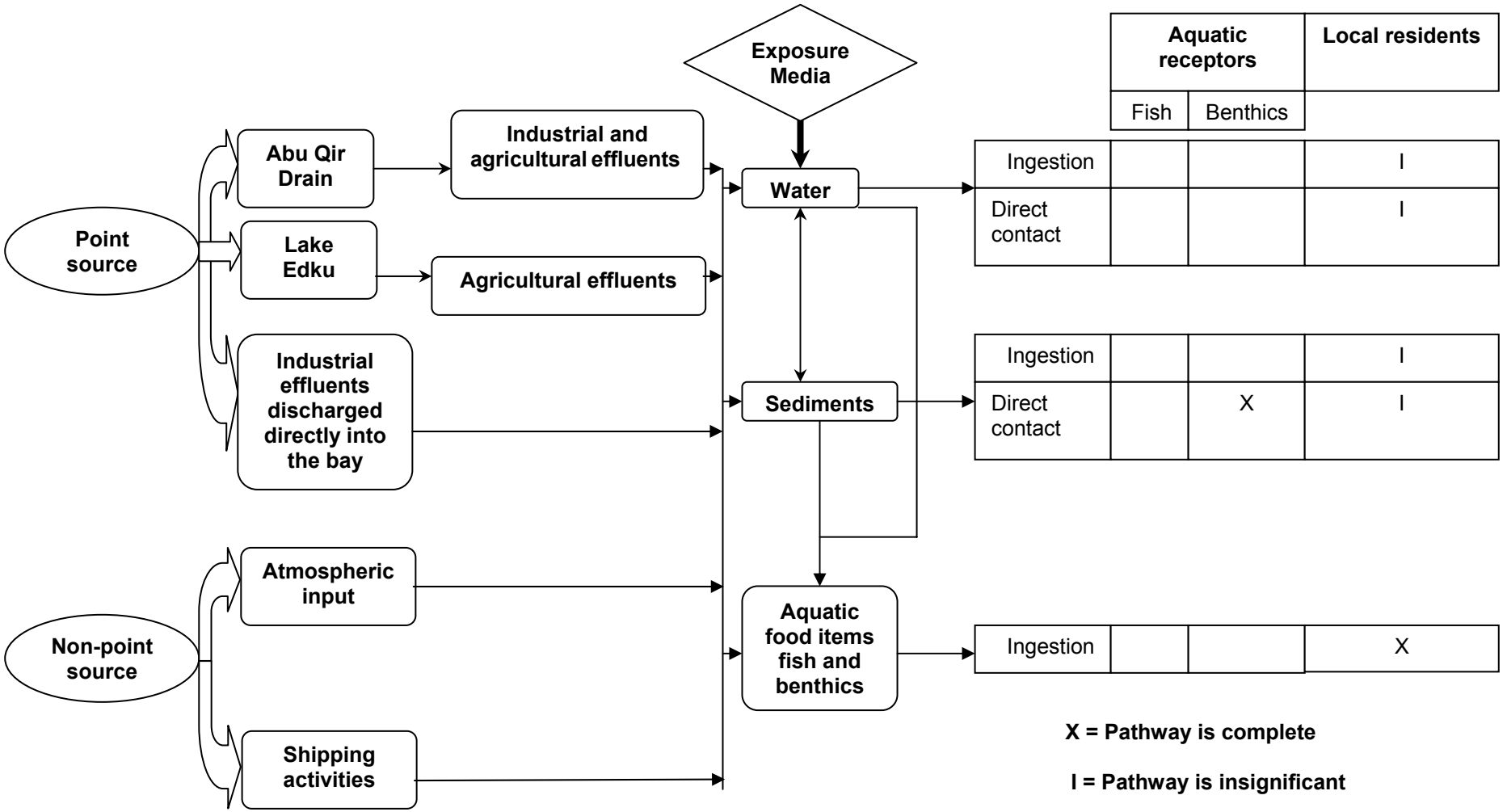


Figure 36: Conceptual site model for the SLRA in Abu Qir Bay.

Table 18: Descriptive statistics of the contaminants evaluated in the SLERA in sediments and bivalves of Abu Qir Bay.

	Sediments		Bivalves			
			Mactra corallina		*Tapes decussata*	
Analyte	**Detection frequency**	**Maximum concentration (mg/kg dw)**	**Detection frequency**	**95 % UCL (mg/kg ww)**	**Detection frequency**	**95 % UCL (mg/kg ww)**
Trace metals						
As	30/30	11.0	7/7	1.76	6/6	1.64
Cr	30/30	186	7/7	2.11	6/6	0.50
Ni	23/30	40.5	NA	NA	NA	NA
Cu	27/30	127	7/7	2.22	6/6	1.89
Zn	30/30	717	7/7	12.2	6/6	12.8
Cd	29/30	3.54	7/7	0.56	6/6	0.33
Se	30/30	4.00	7/7	0.742	6/6	0.660
Hg	30/30	2.70	7/7	0.63	6/6	0.48
Mn	30/30	582	7/7	29.2	6/6	1.67
Pb	30/30	129	7/7	1.73	6/6	1.35
Chlorinated organic compounds						
Analyte	**Detection frequency**	**Maximum concentration (µg/kg dw)**	**Detection frequency**	**95 % UCL (µg/kg ww)**	**Detection frequency**	**Maximum concentration (µg/kg ww)**
HCBz	5/20	22.0	3/7	0.068	2/3	0.073
PCBz	5/20	5.73	2/7	0.042	0/3	<DL
α-HCH	11/20	10.4	4/7	0.531	0/3	<DL
Lindane	14/20	21.5	4/7	0.732	0/3	<DL
Heptachlor	5/20	4.41	3/7	0.178	1/3	<DL
Aldrin	9/20	9.92	0/3	<DL	0/3	<DL
Chlordane	16/20	40.3	7/7	3.18	0/3	<DL
Dieldrin	12/20	18.3	4/7	1.07	0/3	<DL
p,p´DDE	17/20	32.5	7/7	1.87	3/3	0.568
DDD	16/20	78.4	7/7	1.84	2/3	0.229
p,p´DDD	14/20	44.5	7/7	1.02	2/3	0.229
DDT	10/20	9.27	0/3	<DL	0/3	<DL
p,p´DDT	8/20	7.95	0/3	<DL	0/3	<DL
DDTs	17/20	128	7/7	3.90	3/3	0.798
Heptachlor epoxide	13/20	11.8	4/7	0.292	0/3	<DL
Endosulfane	15/20	14.2	7/7	1.04	0/3	<DL
Chlorpyrifos	13/20	41.8	7/7	2.16	1/3	0.059
Methoxychlor	5/20	5.16	3/7	0.445	0/3	<DL
Mirex	5/20	0.824	2/7	0.084	0/3	<DL
PCBs	14/20	22.2	7/7	13.5	3/3	1.83
PAHs						
Analyte	**Detection frequency**	**Maximum concentration (µg/kg dw)**	**Detection frequency**	**95 % UCL (µg/kg ww)**	**Detection frequency**	**Maximum concentration (µg/kg ww)**
Nap	15/20	37.4	7/7	13.0	1/3	8.85
Acy	17/20	25.8	7/7	11.4	1/3	9.26
Ace	14/20	35.6	7/7	10.8	2/3	11.3
Flr	16/20	496	7/7	15.2	1/3	24.5
Phn	17/20	470	7/7	23.1	1/3	52.2
Ant	17/20	211	7/7	15.2	1/3	31.3
LMWPAHs	17/20	1237	7/7	88.0	2/3	137

Table 18: Continued.

	Sediments		Bivalves			
			Mactra corallina		*Tapes decussata*	
Analyte	**Detection frequency**	**Maximum concentration (µg/kg dw)**	**Detection frequency**	**95 % UCL (µg/kg ww)**	**Detection frequency**	**Maximum concentration (µg/kg ww)**
Fla	17/20	357	7/7	34.7	3/3	85.2
Pyr	17/20	490	7/7	31.2	1/3	79.6
BaA	17/20	185	7/7	23.4	1/3	55.0
Chy	17/20	297	7/7	21.8	1/3	62.1
BbF	17/20	109	7/7	25.9	1/3	65.7
BkF	17/20	367	7/7	15.6	1/3	40.3
BaP	17/20	230	7/7	22.7	1/3	54.4
InP	12/20	48.1	7/7	22.9	1/3	52.6
DibA	10/20	75.3	7/7	13.9	1/3	26.5
BghiP	11/20	37.1	7/7	19.2	1/3	42.6
HMWPAHs	17/20	1423	7/7	189	1/3	564
PAHs	17/20	2660	7/7	317	3/3	701

<DL: below the limit of detection

NA: Not available

4.1.3. Effect characterization

Sediments

The effect characterization was based on several sets of sediment quality guidelines (SQGs) reported in literature. These SQGs have been calculated using different theoretical and empirical approaches, such as the equilibrium partitioning (EqP) method (Di Tora et al. 1991; USEPA, 1994), the screening level concentration approach (Neff et al. 1988), the effects range approach including the effect range low (ERL) and the effect range medium (ERM) (Long et al. 1995), the effects level approach (ELA) including the threshold effect level (TEL) and the probable effect level (PEL) (MacDonald et al. 1996), the apparent effects threshold (AET) approach including the apparent effect threshold low (AET-L) and the apparent effect threshold high (AET-H) (Barrick et al. 1988) and the logistic regression models including T20, which represents the probability of occurrence of adverse ecological effects in 20 % of the investigated samples, T50 and T80 (USEPA/NOAA, 2005). In most of the developed sediment quality guidelines, more than one value is available, one representing the low level of adverse ecological effects (ERL, TEL and T20) and the other representing higher level of adverse ecological effects (ERM, PEL, T50 and AET-L). For some sediment quality guidelines, values representing higher level of adverse ecological effects are available (T80 and AET-H), where extreme adverse ecological effects could be expected.

As a result of the different approaches mentioned above, SQGs reported for different pollutants exhibit a great variability, so that some authors have developed the consensus based approach trying to harmonize the existing values (Swartz, 1999; MacDonald et al. 2000a, b), which was used in the present study for the risk calculations and for pointing out the presence of any hot spots in Abu Qir

Bay. Consensus based sediment quality values developed for the investigated pollutants in Abu Qir Bay sediments, together with the sediment quality guidelines used in their calculation are given in **Table 19**. Because consensus based marine SQGs were not available for all the target pollutants, with the exception of PCBs (MacDonald et al. 2000a), values were calculated for all the target pollutants in the present study following the methodology described by MacDonald et al. (2000a, b).

In the consensus approach (CA), consensus-based SQGs are derived from the existing SQGs that have been established for the protection of sediment-dwelling organisms. Derivation of numerical sediment quality guidelines using the CA involves several steps. First, the SQGs for the protection of sediment-dwelling organisms are grouped into two categories according to their original narrative intent, including threshold effect concentrations (TECs) and probable effect concentrations (PECs). TEC group included ERL (Long and Morgan, 1991; Ingersoll et al. 1996a, b), TEL (Smith et al. 1996; Ingersoll et al. 1996 a, b) and T20 (USEPA/NOAA, 2005). The TECs are intended to identify concentrations below which harmful effects on sediment-dwelling organisms are unlikely to be observed. The PECs are intended to identify concentrations above which harmful effects on sediment-dwelling organisms are likely to be frequently or always observed (MacDonald et al. 1996; Swartz, 1999). PEC group included PEL (Smith et al. 1996; Ingersoll et al. 1996a, b), ERM (Long and Morgan, 1991; Ingersoll et al. 1996a), T50 (USEPA/NOAA, 2005) and AET-L (Barrick et al. 1988).

Following classification of the existing SQGs, consensus-based TECs were calculated by determining the geometric mean of the SQGs that are included in this category. Likewise, consensus-based PECs were calculated by determining the geometric mean of the PEC-type values. The geometric mean, rather than the arithmetic mean, was calculated because it provides an estimate of central tendency that is not unduly affected by outliers and because the SQGs may not be normally distributed. Consensus-based TECs or PECs are calculated only if three or more published SQGs are available for a chemical substance or group of substances (MacDonald et al. 2000a, b).

Recent evaluations based on combining several sets of guidelines into one to yield "consensus-based" guidelines have shown that such guidelines can substantially increase the reliability, predictive ability, and level of confidence in using and applying the guidelines (Crane et al. 2000; MacDonald et al. 2000 a, b; Ingersoll et al. 2000). The agreement of guidelines derived from a variety of theoretical and empirical approaches helps to establish the validity of the consensus-based values. Use of values from multiple guidelines that are similar for a contaminant provides a weight-of evidence for relating to actual biological effects. A series of papers were produced (Swartz, 1999; MacDonald et al. 2000a, b) that addressed some of the difficulties associated with the assessment of sediment quality conditions using various numerical sediment quality guidelines. The results of these investigations demonstrated that combining and integrating the effect levels from several sets of guidelines to result in consensus based sediment quality guidelines provide a unifying synthesis of the existing guidelines, reflect causal rather than correlative effects, and can account for the effects of contaminant mixtures in sediment (Swartz, 1999).

Table 19: Summary of the effect concentration levels from different SQGs applied in the SLERA of Abu Qir Bay.

	Threshold effect concentrations				Probable effect concentrations					Extreme effect concentrations		
	ERL	TEL	T20	TEC[a]	ERM	PEL	AET-L	T50	PEC[a]	AET-H	T80	EEC[a]
Trace metals and metalloids (mg/kg dw)												
As	8.20	7.24	7.40	7.60	70.0	41.6	130	20.0	52.5	450	56.0	159
Cd	1.20	0.680	0.380	0.700	9.60	4.21	2.70	1.40	3.50	14.0	4.90	8.30
Cr	81.0	52.3	49.0	59.2	370	160	97.0	140	168	1101	410	672
Cu	34.0	18.7	32.0	27.3	270	108	390	94.0	181	1300	280	603
Pb	46.7	30.2	30.0	34.8	218	112	430	94.0	177	1200	300	600
Hg	0.150	0.130	0.140	0.140	0.710	0.700	1.40	0.480	0.800	2.30	1.70	2.00
Ni	20.9	15.9	15.0	17.1	51.6	42.8	110	47.0	58.1	371	150	236
Zn	150	124	94.0	121	410	271	460	240	333	3800	640	1560
PAHs (µg/kg dw)												
Nap	160	34.6	30.0	55.0	2100	391	230	220	452	2400	1570	1941
Acy	44.0	5.87	14.0	15.3	640	128	130	140	197	2000	1420	1685
Ace	16.0	6.71	19.0	12.7	500	88.9	64.0	120	136	1900	710	1162
Flr	19.0	21.2	19.0	19.7	540	144	120	110	179	3600	660	1541
Phn	240	86.7	68.0	112	1500	544	660	460	706	21000	3060	8016
Ant	63.4	46.9	34.0	46.6	260	245	71.0	290	190	1300	2490	1799
LMWPAHs	552	312	NA	415	3160	1442	1200	NA	1762	29000	NA	29000
Fla	600	113	120	201	5100	1494	1300	1030	1787	30000	8950	16386
Pyr	665	153	120	230	2600	1398	2400	930	1688	16000	6980	10568
BaA	361	74.8	61.0	106	1600	693	960	470	841	5100	3530	4243
Chy	384	108	82.0	150	2800	846	950	650	1100	21000	5190	10440
BbF	NA	NA	130	130	NA	NA	NA	1110	1110	NA	9410	9410
BkF	NA	NA	70.0	70.0	NA	NA	NA	540	540	NA	4120	4120
BaP	430	88.8	69.0	138	1600	763	1100	520	914	3500	3910	3699
InP	NA	NA	68.0	68.0	NA	NA	760	490	610	4400	3480	3913
DibA	63.4	6.22	19.0	19.6	260	135	240	110	175	1900	690	1145
BghiP	NA	NA	67.0	67.0	NA	NA	920	500	678	3200	3710	3446

a: Calculated consensus based SQG for each group calculated according to MacDonald et al. (2000a, b) LMWPAHs: Low molecular weight PAHs

NA: not available

Table 19: Continued.

	Threshold effect concentrations				Probable effect concentrations					Extreme effect concentrations		
	ERL	**TEL**	**T20**	**TEC**	**ERM**	**PEL**	**AET-L**	**T50**	**PEC**	**AET-H**	**T80**	**EEC**
PAHs continued												
HMWPAHs	1700	665	NA	1055	9600	6676	7900	NA	7970	69000	NA	69000
PAHs	4022	1684	NA	2603	44792	16770	NA	NA	27407	NA	NA	NA
PCBs (µg/kg dw)												
PCBs	22.7	21.6	35.0	25.8	**180**	189	450	370	274	3100	3930	3490
Organochlorine pesticides (µg/kg dw)												
HCBz	NA	NA	NA	NA	NA	NA	22.0	NA	22.0	230	NA	230
Lindane	NA	0.320	NA	0.320	NA	0.990	NA	NA	0.990	NA	NA	NA
Heptachlor	NA	NA	NA	NA	NA	NA	1.50	NA	1.50	2.00	NA	2.00
Chlordane	0.500	2.26	NA	1.06	6.00	4.79	2.80	NA	4.32	4.60	NA	4.60
Aldrin	NA	NA	NA	NA	NA	NA	9.50	NA	9.50	NA	NA	NA
Dieldrin	0.020	0.720	0.830	0.229	8.00	4.30	1.90	2.90	3.71	3.50	10.0	5.92
p,p'-DDE	2.20	2.10	3.10	2.43	27.0	374	9.00	100	55.3	62.0	3410	460
DDD	2.00	NA	NA	2.00	20.0	NA	NA	NA	20.0	NA	NA	NA
p,p'-DDD	NA	1.22	2.20	1.64	NA	7.81	28.0	19.0	16.1	63.0	160	100
DDT	1.00	NA	NA	1.00	7.00	NA	NA	NA	7.00	NA	NA	NA
p,p'-DDT		1.19	1.70	1.42	4.77		12.0	11.0	8.57	271	76.0	144
DDTs	1.60	3.90	NA	2.50	4.61	51.7	24.0		38.5	37.0	NA	37.0

HMWPAHs: high molecular weight PAHs

DDT: sum of o,p´-DDT + p,p´-DDT

ERL, ERM (Long et al. 1995)

TEL, PEL (MacDonald et al. 1996)

T20, T50 and T80 (USEPA/NOAA, 2005)

AET-L, AET-H (Barrick et al. 1988)

DDD: sum of o,p´-DDD + p,p´-DDD

DDTs: sum of all DDT isomers and its metabolites

Additionally, MacDonald et al. (2000a) have evaluated the consensus based effect levels for reliability in predicting toxicity in sediments by using matching sediment chemistry and toxicity data from field studies conducted throughout the United States. The results of their evaluation showed that most of the consensus-based threshold effect concentrations (TEC -lower effect level) and probable effect concentrations (PEC - upper effect level) for individual contaminants provide an accurate basis for predicting the absence or presence, respectively, of sediment toxicity.

The consensus-based SQGs as developed only involve effects to benthic macroinvertebrate species. The guidelines do not consider the potential for bioaccumulation in aquatic organisms and subsequent food chain transfers to humans or wildlife. Where bioaccumulative compounds are involved, the consensus-based SQGs need to be used in conjunction with other tools, such as bioaccumulation-based guidelines, bioaccumulation studies, food chain modelling, and tissue residue guidelines to evaluate the direct toxicity and upper food chain effects of these compounds.

Differences in the classification criteria of SQGs used in the present work and those given by MacDonald et al. (2000a) derived small differences in the final consensus based values for total PCBs, although they were of the same order of magnitude (TEC: 25.8 µg/kg dw vs 40 µg/kg dw; PEC: 274 µg/kg dw vs 400 µg/kg dw and EEC: 3490 µg/kg dw vs 1700 µg/kg dw respectively). In any case, the deviations towards the lower values imply a more protective character than those reported previously (conservatism).

Different authors have studied the predictability of the SQGs in relation to false-negative and false-positive classifications. In general, when chemical concentrations are lower than TEC values, the probability of samples correctly classified as non-toxic is higher than 75 % for the target compounds (Long et al. 1995; MacDonald et al. 1996, 2000a). For the PEC values, percentages of success in determining the toxicity of sediment samples are variable, but normally higher than 50 % (Long et al. 1995, 1998; MacDonald et al. 1996, 2000a, b). In the case of the extreme effect concentrations (EECs) in marine sediments, values have been found only for PCBs for which the predictive ability of toxicity was higher than 85 % (MacDonald et al. 2000a). The degree of predictability has also been reported to depend on the type of the toxicity test conducted (Long et al. 1998), the duration of the exposure test (Ingersoll et al. 2000), the level of organization considered (community level vs individual responses) (Hyland et al. 1999) and particularly, to on-site specific environmental factors (Wenning and Ingersoll, 2002; Crane and MacDonald, 2003; Vidal and Bay, 2005).

Pollutants, which were not included in **Table 19** due to the lack of guidelines or the availability of only screening concentrations, were evaluated by comparing the maximum concentration in sediments with this available screening concentration. These screening concentrations represent values below which no adverse ecological effects are expected to occur and above which adverse ecological effects are expected. Pollutants evaluated by this approach include α-HCH, chlorpyrifos, endosulfane (α and β

isomers), heptachlor epoxide, methoxychlor and PCBz. Marine sediment screening concentrations used in the present study for this group are shown in **Table 20**.

Table 20: Marine sediment screening concentrations for organic contaminants.

Analyte	Screening value (µg/kg dw)	Deriving approach	reference
α-HCH	1360	EqP	USEPA, 2004
Chlorpyrifos	8.30	EqP	USEPA, 2004
Endosulfane	0.107	EqP	USEPA, 2004
Heptachlor epoxide	0.600	ISQG	CCME, 2003
Methoxychlor	29.6	EqP	USEPA, 2004
PCBz	191000	EqP	USEPA, 2004

Mussels

Potential risks based on tissue residue data were also evaluated for the bivalves. All toxicity thresholds were identified from the scientific literature. When no toxicity data exists for the selected species in the present study, published data for other species of bivalves were used, which is an acceptable approach in the screening level ecological risk assessment. **Table 21** shows the used toxicity residual concentrations in different mussel tissues, together with the effect class, toxicity measure, exposure route, body part and the life stage. Values shown in **Table 21** were obtained from published papers and from the Environmental Residue Effect Database website (http://el.erdc.usace.army.mil/ered/). In addition, tissue residue concentrations of some target pollutants in both species were compared with tissue screening concentrations (TSCs) developed by Shephard, (1996), which were intended to protect 95 % of all aquatic genera (**Table 22**). TSCs are intended to be nonsite or species specific indicators of tissue residues, which, if not exceeded, pose little threat of adverse risk to aquatic biota. Also concentrations of trace metals in both species were compared to the background concentrations of trace metals in tissues of the Australian oyster (**Table 23**) (Scanes and Roach, 1999).

Table 21: Toxicity data for target pollutants in mussel tissues of different species obtained from literature.

Analyte name	Species scientific name	Species common name	Conc. (mg/kg)	Effect class	Toxicity measure	Exposure route	Body part	Life stage	Reference
Metals									
As	*Mytilus edulis*	Mussel	3.60	Mortality	NOED	Water and ingestion	Whole body	Adult	St-Jean et al. 2003
Cd	*Mytilus edulis*	Mussel	6.45	Mortality	NOED	Water and ingestion	Whole body	Adult	Rule and Aldin, 1996
	Mytilus galloprovincialis	Mediterranean mussel	0.04	Physiological	NOED	Water	Whole body	Larval	Geffard et al. 2002
Cu	*Mytilus galloprovincialis*	Mediterranean mussel	1.00	Physiological	NOED	Water	Whole body	Larval	Geffard et al. 2002
	Mytilus edulis	Mussel	3.40	Mortality	NOED	Water and ingestion	Whole body	Adult	St-Jean et al. 2003
Hg	*Mytilus galloprovincialis*	Mediterranean mussel	169	Biochemical	ED50	Water	Gills	Adult-	Pagliarani et al. 1996
Mn	*Mytilus edulis*	Mussel	9.60	Mortality	NOED	Water and ingestion	Whole Body	Adult	St-Jean et al. 2003
Pb	*Dreissena polymorpha*	Zebra mussel	35.0	Mortality	NOED	Water	Whole Body	Adult	Kraak et al. 1994
Zn	*Mytilus galloprovincialis*	Mediterranean mussel	18.0	Physiological	NOED	Water	Whole body	Larval	Geffard et al. 2002
	Mytilus edulis	Mussel	26.0	Mortality	NOED	Water and ingestion	Whole Body	Adult	St-Jean et al. 2003
PAHs									
Nap	*Mytilus edulis*	Mussel	31.3	Behavior	ED50	Water	Whole Body	Adult	Donkin et al. 1989
Fla	*Mytilus edulis*	Mussel	0.112	Biochemical	NA	Water	Whole body	NA	Ertman et al. 1995
Pyr	*Mytilus galloprovincialis*	Mediterranean mussel	3.40	Cellular	LOED	Water	Whole Body	Adult	Perez-Cadahia et al. 2004
Chy	*Dreissena polymorpha*	Zebra mussel	0.93	Survival	NOED	Water and ingestion	Whole body	Adult	Roper et al. 1997

NOED: no observed effect dose LOED: low observed effect dose ED50: effective dose 50

NA: not available

Table 21: Continued.

Analyte name	Species scientific name	Species common name	Conc. (mg/kg)	Effect class	Toxicity measure	Exposure route	Body part	Life stage	Reference
PAHs continued									
BaP	*Mytilus galloprovincialis*	Mediterranean mussel	21.5	Biochemical	NOED	Ingestion	Whole body	Adult	Akcha et al. 2000
PAHs	*Perna viridis*	Green Mussel	0.08	Biochemical	NOED	Water and ingestion	Liver and gills	Adult	Cheung et al. 2002
PCBs									
PCBs	*Mytilus edulis*	Mussel	0.600	Physiological	NOED	Water and ingestion	Whole body	Adult	Velduizen-Tsoerkan et al. 1991
Pesticides									
Lindane	*Mytilus edulis*	Mussel	0.0136	Behaviour	LOED	Water and ingestion	Whole body	Adult	Hermsen et al. 1994
Endosulfane	*Mytilus edulis*	Mussel	8.1	Mortality	NOED	Water and ingestion	Whole body	Mature	Hermsen et al. 1994
Chlorpyrifos	*Mytilus galloprovincialis*	Mediterranean mussel	4.00	Mortality	NOED	Water and ingestion	Whole body	Adult	Serrano et al. 1995
p,p'-DDE	*Dreissena polymorpha*	Mussel	0.75	Biochemical	NOED	Water	Whole body	NA	Binelli et al. 2006
p,p'-DDD	*Dreissena polymorpha*	Mussel	0.35	Biochemical	NOED	Water	Whole body	NA	Binelli et al. 2005

NA: not available

Table 22: Tissue screening concentrations (mg/kg ww) for the protection of 95 % of aquatic genera (Shephard, 1996)

Analyte name	TSC (mg/kg ww)
As	1.60
Cd	0.042
Cu	0.170
Hg	0.060
Zn	2.80
PCBs	0.44
HCBz	32.0
Aldrin	0.710
Dieldrin	0.009
BaP	416

Table 23: Background concentrations of trace metals (mg/kg ww) in Australian oyster (Scanes and Roach, 1999).

Trace metal	Concentration (mg/kg ww)
As	2.46
Cd	0.73
Cr	0.28
Cu	28.7
Hg	NA
Mn	3.00
Pb	0.12
Se	0.47
Zn	332

NA: not available

4.1.4. Risk characterization

The risk characterization integrates the exposure and effect characterization to assess whether chemical concentrations are sufficiently high to pose unacceptable risks to ecological receptors. It should be emphasized that this SLERA, where possible, incorporated conservatism where uncertainties were apparent, which is typical for a screening analysis (i.e., risks are likely to be overestimated rather than underestimated). This allows for chemicals posing negligible risk to be confidently removed from further evaluations. The chemicals identified as being of potential concern (COPCs) have to be evaluated further in more detailed site-specific assessment to further characterize the risks they pose.

Sediments

In the present study, risk was characterized by comparing the maximum concentration of each pollutant (**Table 18**) with its corresponding sediment quality guideline (**Table 19**). The selected approach was the hazard quotient (HQ). The detailed approach used to evaluate the investigated

contaminants in the SLERA is shown in **Figure 37**. Two HQs were calculated for each pollutant; TEC HQ, which was calculated by dividing the maximum concentration of each pollutant by the calculated consensus-based TEC ($CBSQG_{TEC}$) and the PEC HQ, which was calculated by dividing the maximum concentration of each pollutant by the calculated consensus-based PEC ($CBSQG_{PEC}$) (**Figure 37**). When TEC HQ < 1 for a given pollutant, rare adverse ecological effects are expected to occur with respect to this pollutant, when PEC HQ > 1, frequent adverse ecological effects are expected to occur and when TEC HQ > 1 > PEC HQ, adverse ecological effects are possible but less frequent than the previous level (**Figure 37**)

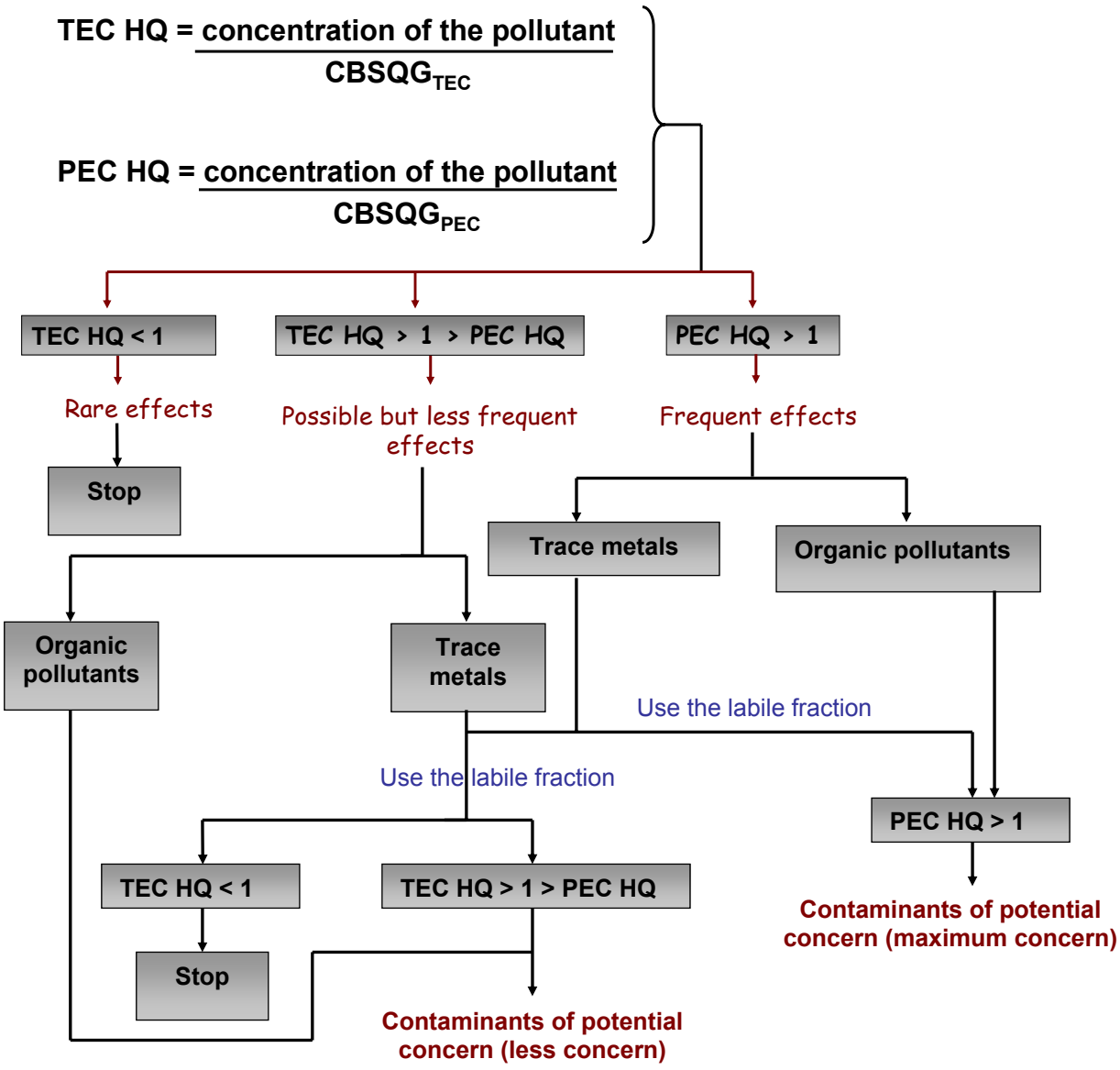


Figure 37: SLERA approach applied in Abu Qir Bay.

Trace metals were further evaluated by calculating both HQs (TEC HQ and PEC HQ) based on the concentration of the labile fraction (the sum of the first 4 fractions obtained from the sequential extraction scheme).

Calculated HQs for the investigated trace metals in the bay sediments are shown in **Figure 38**. As shown in the figure, TEC HQ calculated for all the investigated trace metals were higher than 1 (**Figure 38a**). At the same time, calculated TEC HQ for Cr, Cu, Ni, Pb and Zn based on the labile fraction of each element were higher than 1 indicating the possibility of occurrence of adverse ecological effects to benthic organisms. Based on the calculated values of PEC HQ (**Figure 38b**), it can be recognized that Cd, Cr, Hg and Zn had values higher than one based on the total metal concentration. On the other hand, when the labile fraction was used as the exposure concentration, only Zn had PEC HQ higher than one. Thus it can be concluded that frequent adverse ecological effects are expected to occur with respect to Zn, Cd and Hg and that adverse ecological effects are possible but less frequent with respect to As, Cr, Cu, Ni and Pb.

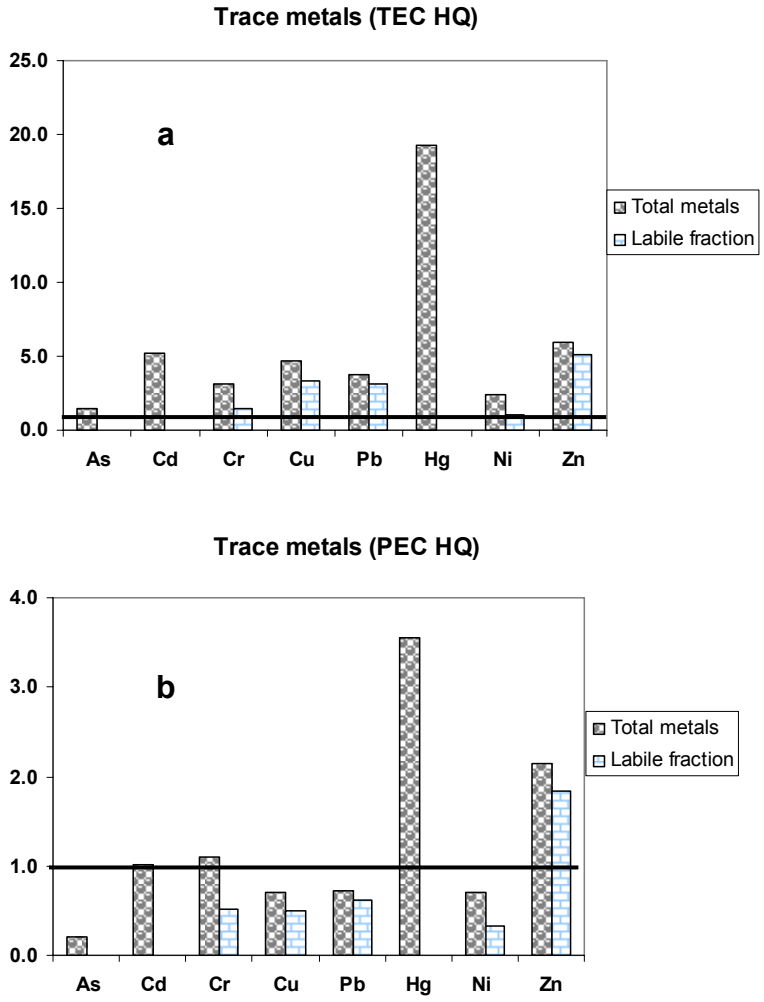


Figure 38: TEC HQ (a) and PEC HQ (b) for trace metals in Abu Qir Bay sediments.

Calculated HQs for the investigated trace organic pollutants are shown in **Figure 39**. It can be seen that except for PCBs, all the organochlorine pesticides (dieldrin, γ-HCH, DDTs, chlordane, DDD, p,p'-DDD, p,p'-DDE, DDT and p,p'-DDT) had TEC HQ values higher than 1 (**Figure 39a**). But only dieldrin, γ-HCH, DDTs, chlordane, DDD, p,p'-DDD and heptachlor had PEC HQ values higher than 1 indicating greater possibility of occurrence of adverse ecological effects with respect to these organochlorine pesticides.

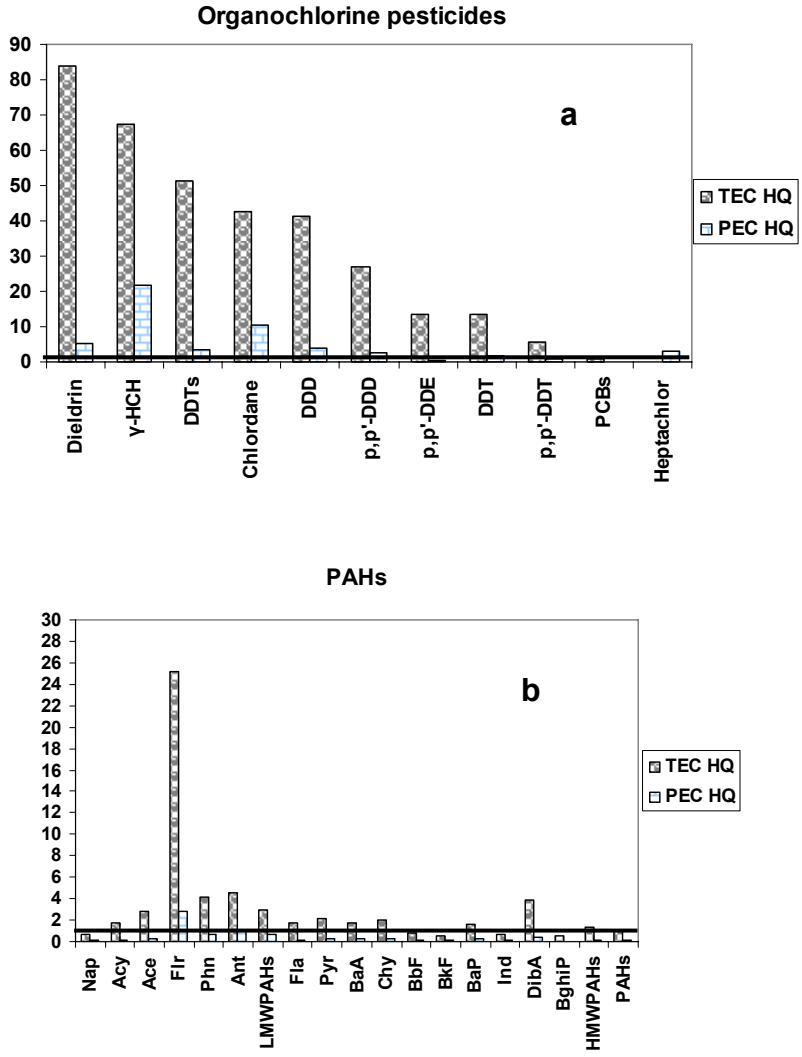


Figure 39: TEC HQ and PEC HQ for chlorinated organic compounds (a) and PAHs (b) in sediments of Abu Qir Bay.

Based on the calculated values of TEC HQ for PAHs, all the lower molecular weight PAHs (LMWPAHs), except Nap had TEC HQ > 1. At the same time, the higher molecular weight PAHs (HMWPAHs) such as Fla, Pyr, BaA, Chy and BaP had TEC HQ > 1 (**Figure 39b**) indicating the possibility of occurrence of adverse ecological effects. But only Flr and Ant had PEC HQ > 1 and thus more possibility of occurrence of adverse ecological effects.

A problem occurred when evaluating the possibility of occurrence of adverse ecological effects related to aldrin and HCBz. No TEC level is available for both organochlorine pesticide and when the maximum concentration of each one was compared with the PEC, the resulting PEC HQ was lower than one in both cases, but this only indicates that adverse ecological effects are not frequently expected. Thus further investigations are required to determine the extent of adverse ecological effects associated with the exposure to HCBz and aldrin in the bay sediments.

As shown earlier, some of the investigated organochlorine pesticides were evaluated by comparing the maximum concentration with the sediment screening concentration developed by USEPA, (2004) (**Table 20**). It was found that all the concentrations of PCBz, methoxychlor and α-HCH in sediments of Abu Qir Bay were lower than the screening concentration for each, which may indicate that adverse ecological effects are unlikely to occur. On the other hand, all detected concentrations of endosulfane in the bay sediments were much higher than the screening concentration in **Table 20**, which may indicate that adverse ecological effects are more likely to occur with respect to endosulfane. For heptachlor epoxides, most of the investigated samples (except 2 samples), where epoxides were detected showed higher values than the screening concentration. In the case of chlorpyrifos four of the investigated sediment samples (in front of AQD and the Maadeya Outlet) showed higher concentrations than the screening benchmark for this pollutant. Thus it can be concluded that adverse ecological effects are expected to occur or possible with respect to chlorpyrifos and heptachlor epoxides. The absence of a higher screening value (like PEC) makes it difficult to determine the extent of adverse effect expected to occur from these pollutants.

Evaluation of the adverse ecological risk usually includes the calculated HQ based on the maximum concentrations in the first stage, followed by determining the number of samples exceeding the used quality guidelines to determine contaminants of potential concern in a given area. Maximum detected TEC HQ and PEC HQ, together with the percentage of samples exceeding TEC and PEC level are given in **Table 2**4. As shown in **Table 24**, investigated pollutants (organics and trace metals) are divided into two groups: group 1 that included lindane, dieldrin, chlordane, DDTs, DDD, DDT, heptachlor, Flr, Ant, Cd, Cr and Zn was characterized by the maximum possibility of occurrence of adverse ecological effects when benthic organisms are exposed to these pollutants in the bay sediments (PEC HQ > 1). It was also found that detected concentrations of chlordane were higher than extreme effect concentration (EEC) in 45 % of the samples and in 20 % of the samples in dieldrin and heptachlor indicating higher probability of adverse effects. For all the target pollutants in this group (except for Flr), the maximum calculated PEC HQ was always located in front of the major sources of pollution (Abu Qir Drain or the Maadeya Outlet). It was only Flr, which showed the maximum HQ value in station 27 (harbour area), which had the maximum concentration of PAHs in the bay sediments. Except for Cr, Flr and Ant, pollutants in this group could be considered as contaminants of the maximum ecological concern, and hence should be given the priority for further investigated in a more detailed ecological risk assessment using site specific toxicity investigation.

Table 24: Summary of the informations obtained from the risk characterization process for pollutants in sediments of Abu Qir Bay.

Analyte name	Metal type	Maximum PEC HQ	Location of the maximum PEC HQ	Percentage of exccedance of PEC HQ	Percentage of exccedance of TEC HQ
Group 1					
Lindane		21.7	Station 1 (in front of AQD)	45 % (n = 20)	10 %
Chlordane		10.6		45 % (n = 20)	20 %
Hg		3.37	Station 2 (in front of Fertilizer Company)	43 % (n = 30)	57 %
Dieldrin		5.17	Station 1 (in front of AQD)	30 % (n = 20)	30 %
DDD		4.13		25 % (n = 20)	35 %
DDTs		3.32		25 % (n = 20)	40 %
Heptachlor		3.00	Station 4 (in front of Maadeya Outlet)	25 % (n = 20)	NA
DDT		1.91		10 % (n = 20)	20 %
Flr		2.77	Station 27 (western part)	5 % (n = 20)	0
Ant		1.11		5 % (n = 20)	0
Zn	Total	2.15	Station 2 (in front of Fertilizer Company)	3 % (n = 30)	10 %
	Labile	1.84		33 % (n = 9)	33 % (n = 9)
Cd	Total	1.01		3 % (n = 30)	57 %
	Labile	NA		NA	NA
Cr	Total	1.11		3 % (n = 30)	13 %
	Labile	0.52		0	11 % (n =9)
Group 2					
Analyte name		**Maximum TEC HQ**	**Location of the maximum TEC HQ**		
p,p'-DDE		13.4	Station 2 (in front of Fertilizer Company)		45 %
p,p'-DDT		5.59	Station 1 (in front of AQD)		25 %
As	Total	1.45	Station 2 (in front of Fertilizer Company)		6.7 % (n = 30)
	Labile	NA			NA
Cu	Total	4.65			17 % (n = 30)
	Labile	3.34			17 % (n = 30)
Pb	Total	3.70			33 % (n = 30)
	Labile	3.16			13 % (n =9)
Ni	Total	2.37			27 % (n = 30)
	Labile	1.08	Station 14 (in front of the Wepco Company seaward)		33 % (n = 9)
Acy		1.68	Station 27 (western part)		35 % (n = 20)
Ace		2.81			
Phn		4.19			5 % (n = 20)
LMWPAHs		2.99			
Fla		1.77			10 % (n = 20)
Pyr		2.13			
BaA		1.75			5 % (n = 20)
Chy		1.97			
BaP		1.67			5 % (n = 20)
DibA		3.85			10 % (n = 20)
HMWPAHs		1.35			5 % (n = 20)
PAHs		1.04			

NA: not available

Cr was not given the same priority as that of this group because when the labile fraction was used as the basis for the HQ calculation, only one sample (station 2) had TEC HQ >1 >PEC HQ and all the other stations showed TEC HQ < 1, thus it can be excluded from further investigations. Flr and Ant were also excluded because only one sample showed the possibility of occurrence of adverse ecological effects (**Table 24**).

The second group included As, Pb, Ni, Cu, PAHs, p,p´-DDE, p,p´-DDT and most of the individual PAHs. This group was characterized by concentrations between TEC level and the PEC level (TEC < concentrations < PEC) in some of the investigated sediment samples. Pollutants in this group can be arranged in the following descending order based on the number of samples which showed TEC < concentration < PEC represented as percentage: p,p´-DDE (45 %) > Pb (33 %) > Ni (27 %) > p,p´-DDT (25 %) > Cu (17 %) > As (6.7 %) > PAHs (5 %). For the individual PAHs, 10 of the 16 investigated PAHs can be located in this group and can be arranged in the following descending order based on the number of samples which showed TEC < concentration < PEC represented as percentage: Ace, Acy (35 %) > Ant (20 %) > Fla, Pyr, DibA (10 %) > Phn, BaA, Chy, BaP (5 %). Occurrence of concentrations between TEC level and PEC level represent sediments in which toxicity is possible but less probable than the first group and that toxicity is uncertain to which extent adverse effects could appear. Most of the pollutants located in this group could be considered as contaminants of potential concern but to a lesser degree when compared to the first group. A decision has to be taken whether these pollutants should be included in a detailed level risk assessment or not. Arsenic (As) and PAHs could be screened out because only two samples in the case of As and one sample in PAHs showed concentrations between TEC and PEC.

PCBs and some of the individual PAHs such as Nap, BbF, BkF, InP and BghiP showed TEC HQ values lower than 1 in all the investigated sediment samples and thus rare adverse ecological effects are expected to occur with respect to these pollutants. In consequence, these pollutants should not be examined in a detailed risk assessment.

4.1.5. Areas of special concern based on the conducted SLERA

One of the principle goals of conducting this screening ERA was the identification of sites of special concern in the bay due to the occurrence of the different investigated pollutants. The application of the HQ methodology is appropriate for the screening level assessment and may provide a good visualization tool or risk indicator for sites. The HQ was estimated by means of the two approaches considered in the present study (TEC HQ and PEC HQ). Calculated values for each pollutant in the investigated sediment samples are shown in **Figure 40**. It can be observed that generally the highest risk for adverse ecological effects (PEC HQ > 1) from sediments was located in front of the AQD, the Fertilizer Company and the Maadeya Outlet and thus can be regarded as hot spots.

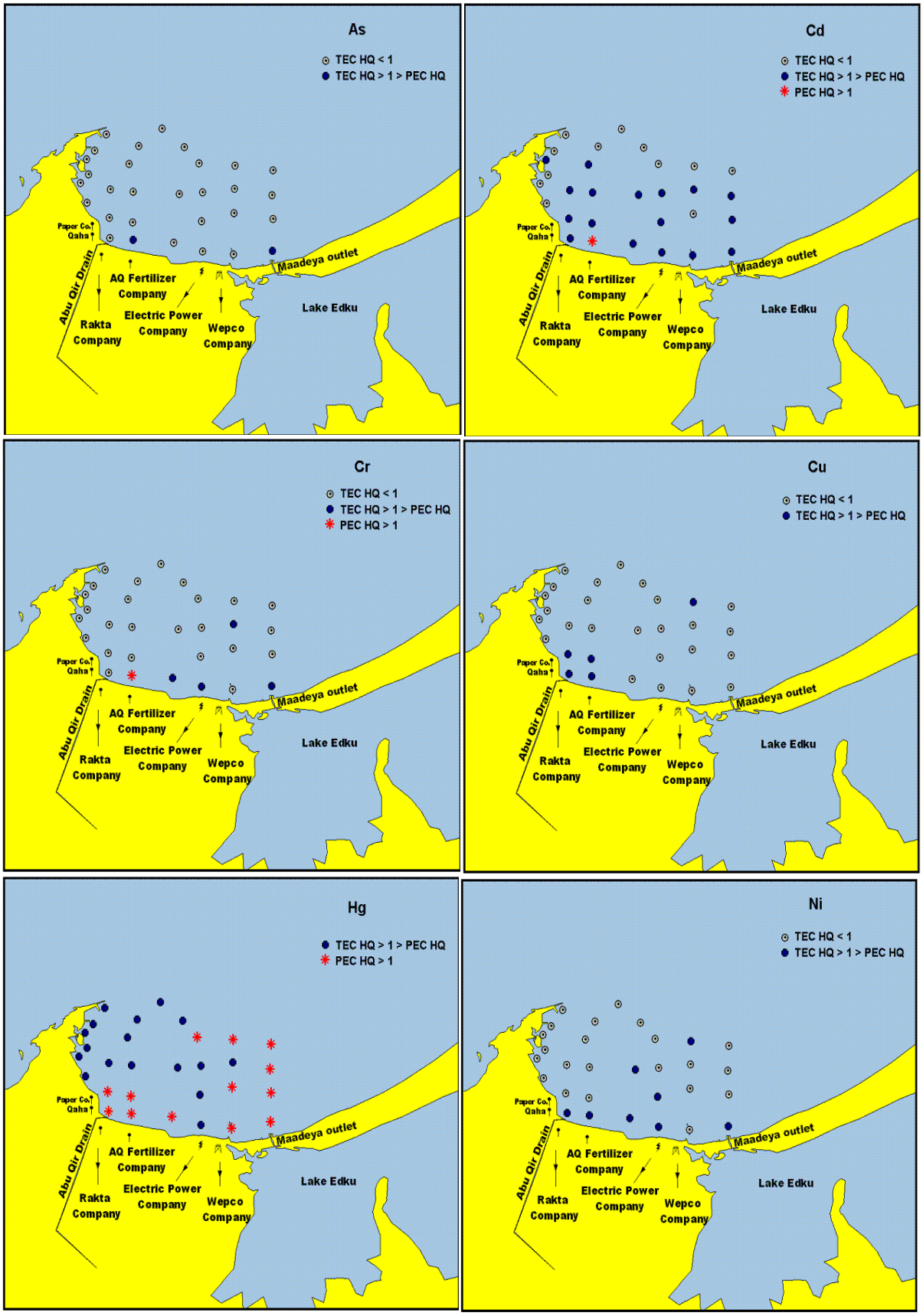


Figure 40: Geographical distribution of HQ in Abu Qir Bay sediments.

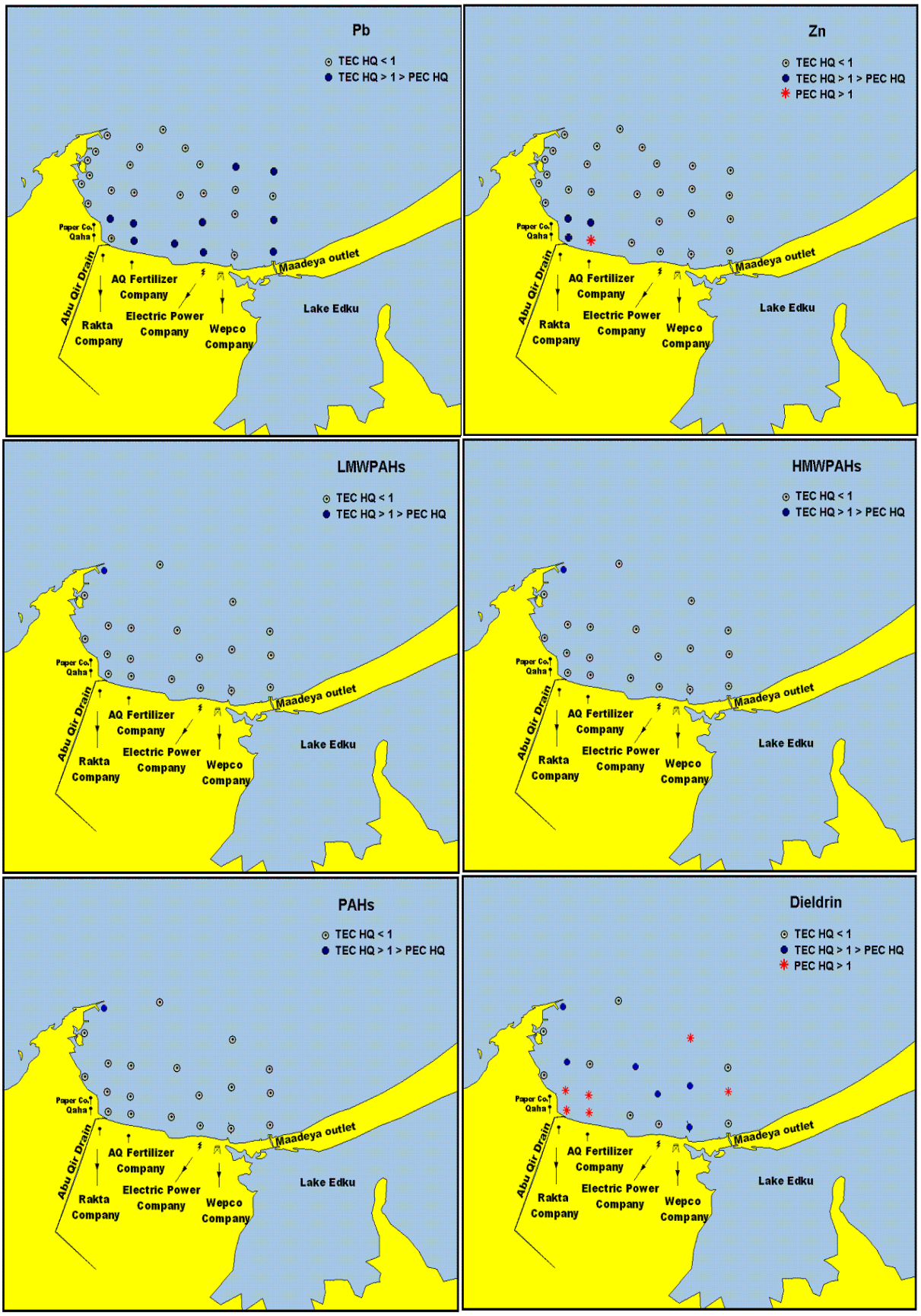


Table 40: Continued.

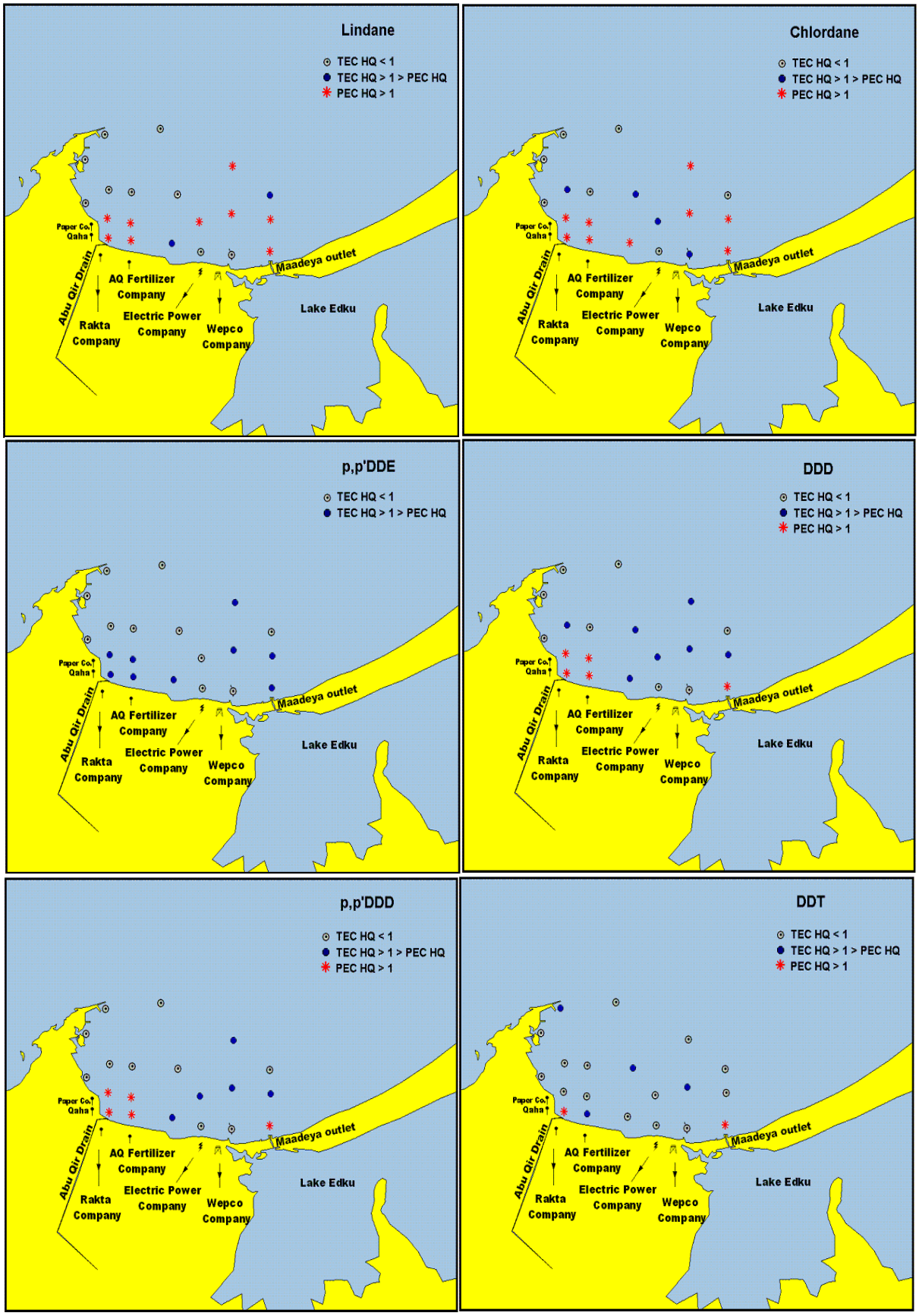


Figure 40: Continued.

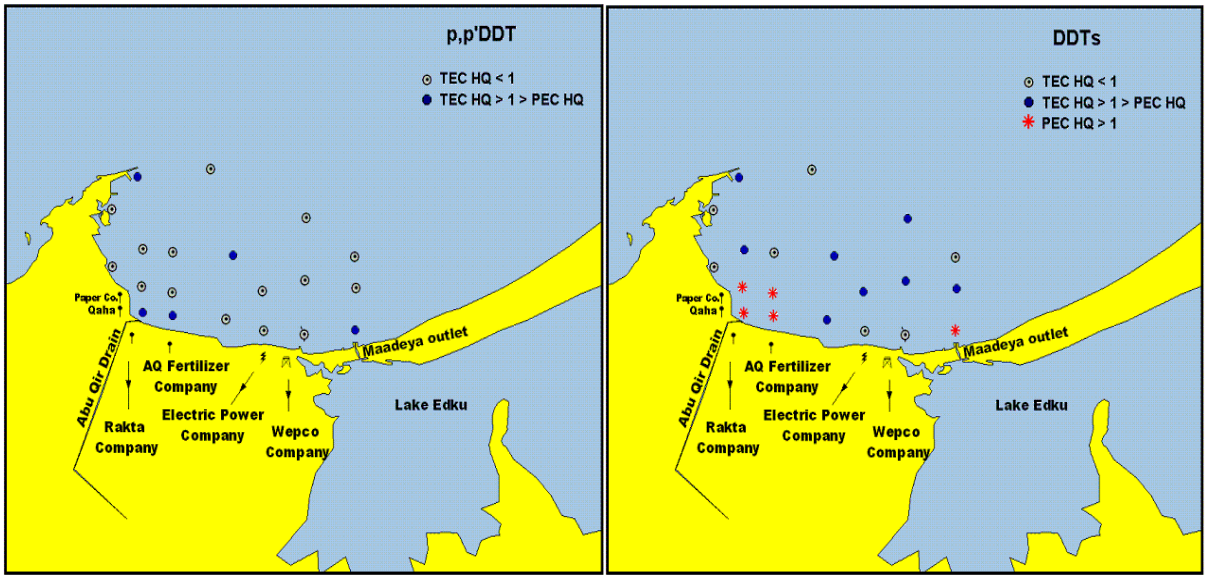


Figure 40: Continued.

The highest values of PEC HQ for most of the investigated pollutants were observed in AQD region and thus more risk is expected as higher values of PEC HQ indicated higher risk (MacDonald et al. 2000). Almost all the trace metals showed PEC HQ > 1 in sediments of station 2 (**Figure 40**). In case of Hg, larger number of samples showed PEC HQ > 1, which was distributed in different parts of the bay. At the same time, all the other samples had Hg concentrations between the TEC and the PEC, which may indicate that adverse ecological effects are expected to occur in almost the whole bay and that the extent of effects should be the highest in front of AQD and the Maadeya Outlet.

Looking at **Figure 40**, one can also realize that most of the ecological effects are expected to occur by the organochlorine pesticides (dieldrin, chlordane, lindane and DDTs) as the number of samples which showed PEC HQ > 1 were higher compared to the trace metals especially in front of AQD and Maadeya Outlet. Due to the circulation pattern of water discharged from the Maadeya Outlet, some other locations (stations 12, 13 and 14) showed also possibility of occurrence of adverse ecological effects especially for dieldrin, lindane and chlordane.

In summary, pollutants in sediments of the AQD region were found to cause the maximum adverse ecological effects to benthic organisms. The absence of bivalves at AQD region may be related to the results of this SLERA.

Mussels

Unfortunately, no toxicity data were available for the two investigated species in literature. Thus detected concentrations of the different pollutants in the tissues of the two mussel species were compared with the toxicity data of other mussel species either in the Mediterranean Sea or in other parts worldwide (**Tables 21, 22 and 23**). The comparison was limited to the available database. This

extrapolation is generally accepted in the SLERA (USEPA, 1992). Comparisons are shown in **Figure 41**. If the detected concentrations of pollutants in tissues of the two mussel species were compared with the toxicity reference concentrations developed by Shephard (1996) for the protection of 95 % of the benthic species, one can observe that As, Cd, Cu, Hg and Zn concentrations in both species were higher than the reference values, which could give an indication of the probability of occurrence of adverse ecological effects (**Figure 41a**). On the other hand, all detected concentrations of trace organic pollutants (with an established TRC) were lower than the toxicity reference concentrations. The comparison of PAH concentrations in the two mussel species with the available toxicity data as an example of the organic pollutants are shown in **Figure 41b**. Comparing trace metal concentrations with the background metal concentrations in Australian oyster, it can be recognized that Cr, Pb and Mn concentrations are higher than the background oyster concentrations (**Figure 41a**).

As, Cd, Cu and Zn concentrations recorded in tissues of both species in the present study were lower than concentrations that caused mortality in *Mytilus edulis* (**Figure 41a**). At the same time, concentrations of Hg and Zn were lower than concentrations in the Mediterranean mussel (*Mytilus galloprovincialis*) which were reported to cause biochemical and physiological effects respectively. It was only Mn in *Mactra corallina*, which showed concentrations higher than the concentration causing mortality in *Mytilus edulis*. At the same time, all the detected concentrations of trace organic pollutants (with reported toxicity data) in both species were lower than concentrations causing different effects in different mussel species (**Table 21**).

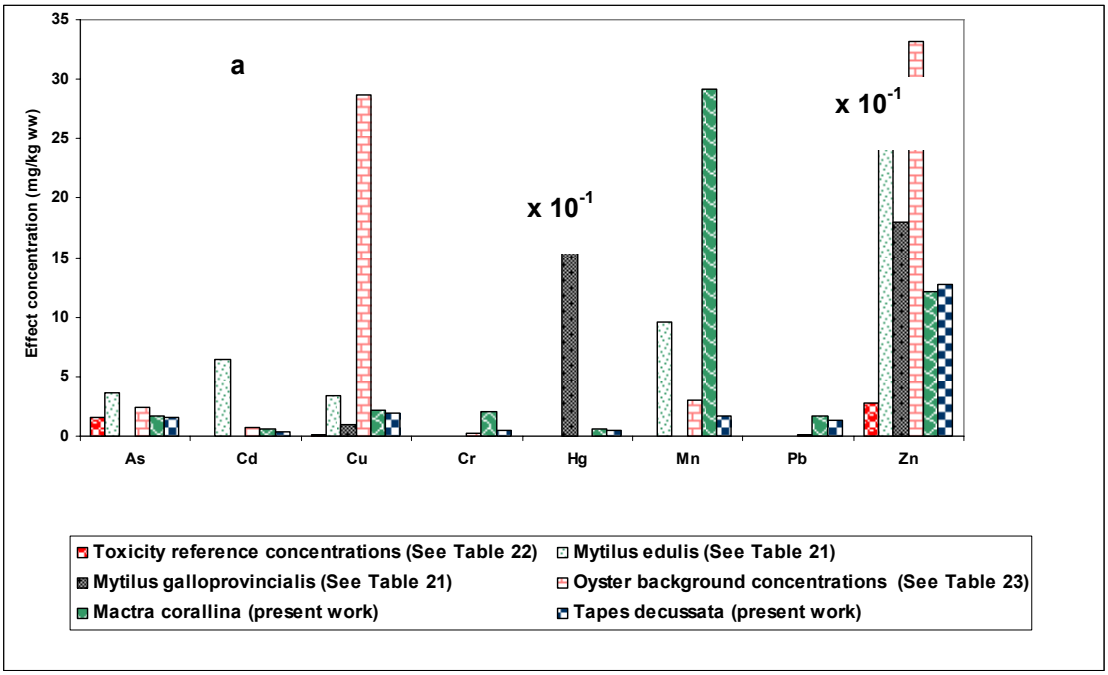


Figure 41: Tissue concentrations of trace metals (a) and PAHs (b) in *Mactra corallina* and *Tapes decussata* investigated in the present work compared to toxicity concentrations reported in literature.

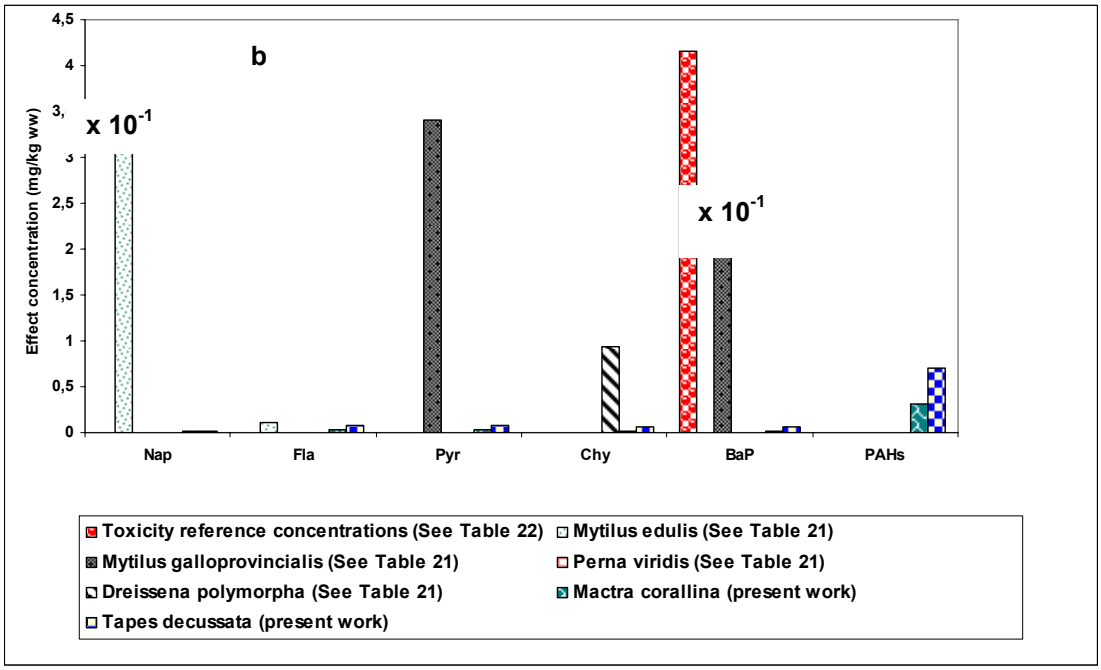


Figure 41: Continued.

4.2. Human health risk assessment (HHRA)

Human Health Risk Assessment (HHRA) is a tiered process that progresses from the use of short-term tests (acute oral and dermal toxicity, skin and eye irritation, mutagenicity, sensitisation potential) and conservative assumptions to longer-term (chronic) tests paired with more realistic assumptions. The purpose of this assessment was to investigate the likelihood that adverse health effects could occur in local residents as a result to the ingestion of the mussel tissues, which were sampled from Abu Qir Bay.

In **Figure 36**, the conceptual model developed for Abu Qir Bay showed all the possible exposure pathways and exposure routs regarding the local residents as the ingestion of water, sediments and food. Here, the only selected exposure route was by consumption of the two mussel species investigated in the present study. It must be pointed out that fishermen represent a great portion of the local residents in Abu Qir region. Dermal contact with sediments and the accidental ingestion of sediments were not included in the present study because Abu Qir Bay is no longer regarded as a recreational area after closing the main beach almost two years ago. So ingestion of sediments and water or dermal contact with both mediums is unlikely.

4.2.1. Intake assumption

Generally the intake or dose of a particular chemical by a receptor is calculated with the equation:

$$I = \frac{C \times CR}{BW} \times \frac{Ef \times ED}{AT}$$

Where:

I = intake (mg kg^{-1} BW day^{-1})
C = concentration of a compound in the medium (mussel tissues)
CR = contact rate or the amount of impacted medium contacted per event (average ingestion rate).
Ef = exposure frequency (days $year^{-1}$)
ED = exposure duration
BW = mean body weight (kg)
AT = average timing (days)

This equation calculates an intake that is normalized over the body weight of the individual and the duration of exposure.

4.2.2. Exposure assessment

Two different types of health effects are considered in the present study: nonthreshold (carcinogenic) effects and threshold (noncarcinogenic) effects. For carcinogenic effects, the relevant intake is the total cumulative intake averaged over a lifetime, because the quantitative dose-response function for carcinogens is based on the assumption that cancer results from cumulative lifetime exposure to carcinogenic agents. Thus for potentially carcinogenic chemicals, the averaging time (AT) is equal to 70 years (USEPA, 1997a).

Noncarcinogenic effects were evaluated for potential chronic exposures in the present study. The relevant intake or dose was based on the daily intake averaged over the exposure period. The quantitative dose-response function for noncarcinogenic effects is based on the assumption that effects occur once a threshold dose is attained (USEPA, 1989). For noncarcinogenic effects, the averaging time (AT) is equal to the period of exposure for the receptor.

The intake or dose for the ingestion of mussels is calculated based on the equation (USEPA, 1989; USEPA, 1997a):

$$CDI = \frac{C_{tis} \times Rf \times IR \times Cf \times ABS \times Ef \times ED}{BW \times AT}$$

Where:

CDI = chronical daily intake (mg kg^{-1} day^{-1})
C_{tis} = concentrations (mg/kg wet weight) of the investigated chemical pollutants in bivalve tissues
Rf = reduction factors (unitless)
IR = ingestion rate (g day^{-1})
Cf = conversion factor (10^{-3} kg/g)

ABS = ingestion absorption factor (fraction absorbed)
Ef = exposure frequency (days $year^{-1}$)
ED = exposure duration (years)
BW = body weight (kg)
AT = average time of exposure (days)

The reduction factor is a number between 0 and 1 that describes the fraction of the pollutants originally that remains after the mussels have been cooked. As this reduction value was not known for the two investigated mussel species, a factor of 1 was used as a conservative assumption. The absorption factors (ABS) is the fraction of pollutants absorbed during ingestion and is specific. In general, it is assumed to be 100 %, which is conservative and thus 100 % ABS was used in the present study. The ingestion rate (IR) for mussels was obtained from a study performed on Egypt (FAO, 2005). All the other parameters used in the equation were default values obtained from the USEPA documents USEPA, 1989, 1991, 197a). Values used in the present study to calculate the CDI are summarized in **Table 25**.

Table 25: Parameters used for the calculation of the CDI in the exposure characterization step.

Parameter	Value	Reference
IR	0.27 g/day	FAO, 2002
ABS	100 %	Conservatively assumed
Ef	365 days/year: carcinogenic 350 days/year: non-carcinogenic	USEPA, 1989 USEPA, 1991
ED	Carcinogenic lifetime: 70 years Non-carcinogenic: 30 years	USEPA, 1989 USEPA, 1991
BW	70 kg	Default body weight of an adult USEPA, 1997a
AT	Carcinogenic effects: 365 x 70 days Noncarcinogenic effects: 365 x 30 days	USEPA, 1989
Rf	1	Conservatively assumed

4.2.3. Toxicity assessment

The purpose of this part is to identify the relationships between the magnitude of contaminants to which receptors are exposed (dose) and the likelihood of an adverse health effect (response). Both carcinogenic and noncarcinogenic health effects are considered in the dose-response assessment. The information provided in the dose-response assessment is combined with the results of the exposure assessment to provide an estimate of potential health risk.

Dose-response information used in this risk assessment was provided in the EPA's Integrated Risk Information System (IRIS) (www.epa.gov/iris) (USEPA, 1998) or Health Effects Assessment Summary Tables (HEAST) (USEPA, 1997b) (http://rais.ornl.gov/cgi-bin/tox/TOX_select?select=nrad).

Noncarcinogenic dose-response

Compounds with known or potential noncarcinogenic effects are assumed to have a dose below which no adverse effects occur or conversely, above which an effect may be seen. This dose is called the threshold dose. In laboratory experiments, this dose is known as the no observed adverse effect level (NOAEL). In the absence of NOAEL, the lowest observed adverse effect level (LOAEL) can be used. By applying uncertainty factors to the NOAEL or the LOAEL (**Appendix II, Table A3**), the USEPA has developed reference doses (RfDs) and reference concentrations (RfCs) for oral and inhalation exposures to compounds with potential noncarcinogenic effects (USEPA, 1998). RfDs and RfCs are available for chronic, subchronic, and in some cases acute exposures in IRIS or HEAST.

A chronic RfD is defined as an estimate (with uncertainty spanning perhaps an order of magnitude or greater) of a daily exposure level for the human population including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during a lifetime. Prior to the development of RfDs, noncarcinogenic effects of chronic exposures were evaluated using values called acceptable daily intake (ADI), which was adopted by the joint FAO/WHO meeting on pesticides and residues (JMPR). ADIs and RfDs are similar in concept. In the present study, RfDs were used because they were available online and the detailed methodology used in their derivation was supported. According to the USEPA, RfDs have been reviewed and verified by an intra-agency RfD workgroup, and thus they are preferred over other values that have not undergone such review.

Uncertainty factors account for uncertainties associated with the dose-response value, extrapolating from the high doses used in the laboratory experiment to the low doses typically encountered in environmental settings, and evaluating sensitive subpopulations. RfDs are expresses in terms of mg kg^{-1} body weight day^{-1}. A summary of the toxicological data for noncarcinogenic pollutanrs given by IRIS and which are used in the present study are shown in **Appendix II, Table A3**.

Carcinogenic dose-response

For carcinogenic effects, USEPA uses a two-step evaluation in which the chemical is assigned a weight of evidence classification, and then an oral cancer slope factor is calculated. The weight of evidence classification is based on the likelihood of compounds being a human carcinogen. Group A compounds are classified as human carcinogens, group B (B1 indicates that limited human data are available and B2 indicates sufficient evidence in animals but inadequate or no evidence in humans) compounds are probable human carcinogens, group C compounds are possible human carcinogens, group D compounds are not classified as human carcinogens and Group E compounds have evidence of noncarcinogenicity for humans.

In the second part of evaluation, cancer slope factors are calculated for compounds that are known or probable human carcinogens. Generally the oral slope factor (OSF) is a plausible upper-bound estimate of the probability of the development of cancer in an individual as a result to the exposure to

a particular level of potential carcinogen. The USEPA developed mathematical models that extrapolate observed responses at high dose or concentrations used in animal studies to predict responses in humans at the low doses or concentrations encountered in environmental situations. The models developed by the USEPA assume no threshold and usually use animal as well as human data to develop an estimate of the carcinogenic potency of a compound. Oral cancer slope factors are expressed in terms of $(mg/kg\text{-}day)^{-1}$, which represents the risk per average daily dose in mg/kg-day. A summary of the toxicological data for carcinogenic pollutants given by IRIS and which are used in the present study are shown in **Appendix II, Tables A**4.

4.2.4. Risk characterization

Potential noncarcinogenic effects were evaluated by calculating a chronic hazard quotient (HQ). For a single compound, the hazard quotient (HQ) is the ratio of the CDI to a reference dose:

$$HQ = \frac{CDI}{RfD}$$

As the RfD reference dose is a threshold dose or intake, which is conservatively chosen so that if the estimated intake is less than the reference dose (HQ<0.1), there is almost no possibility of an adverse health effect. However if the intake exceeds the reference dose (HQ>0.1), this doesn't indicate an adverse health effect is expected, only that a conservative threshold is exceeded.

Carcinogenic effects were quantified by estimating the probability of contracting cancer based on a site related exposure. Cancer risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to a potential carcinogen. In order to estimate the cancer risk, the CDI is multiplied by the cancer oral slope factors (OSF) of the chemical investigated as shown in the following equation:

$$Risk = CDI \times OSF$$

USEPA under superfund uses a risk level of 10^{-6} as the point at which risk management decisions can be considered. Risk management decisions most frequently made under superfund are in the cancer risk range of 10^{-6} to 10^{-4} (USEPA, 1996b).

Assessment of health effects

Table 26 shows the reference doses (RfDs) from IRIS and the CDI calculated for the noncarcinogenic effects for each pollutant. Calculated CDI for carcinogenic effects, together with the OSFs are shown in **Table 27**. Calculated HQs and cancer risks for the investigated pollutants in both species are summarized in **Table 28**.

Table 26: RfDs given by EPA and CDI (noncarcinogenic) for mussels collected from Abu Qir Bay.

Analyte	RfD mg kg^{-1} day^{-1}	Data origin	CDI *Mactra corallina*	CDI *Tapes decussata*
As	3×10^{-4}	IRIS	6.51×10^{-6}	6.07×10^{-6}
Cd	1×10^{-3}	IRIS	2.07×10^{-6}	1.22×10^{-6}
Cr	1.5	IRIS	7.80×10^{-6}	1.85×10^{-6}
Cu	4×10^{-2}	HEAST	8.21×10^{-6}	6.99×10^{-6}
Hg	1×10^{-4}	IRIS	2.33×10^{-6}	1.78×10^{-6}
Mn	1.4×10^{-1}	IRIS	1.08×10^{-4}	6.18×10^{-6}
Pb	3.6×10^{-3}	WHO, 2000	6.40×10^{-6}	4.99×10^{-6}
Se	5×10^{-3}	IRIS	2.74×10^{-6}	2.44×10^{-6}
Zn	3×10^{-1}	IRIS	4.51×10^{-5}	4.73×10^{-5}
PCBs	1×10^{-2}	IRIS	4.99×10^{-8}	6.77×10^{-9}
Nap	2×10^{-2}	IRIS	4.81×10^{-8}	3.27×10^{-8}
Ace	6×10^{-2}	IRIS	3.99×10^{-8}	4.18×10^{-8}
Flr	4×10^{-3}	IRIS	5.62×10^{-8}	9.06×10^{-8}
Phn	3×10^{-1}	IRIS	8.54×10^{-8}	1.93×10^{-7}
Ant	3×10^{-1}	IRIS	5.62×10^{-8}	1.16×10^{-7}
Fla	4×10^{-3}	IRIS	1.28×10^{-7}	3.15×10^{-7}
Pyr	3×10^{-2}	IRIS	1.15×10^{-7}	2.94×10^{-7}
BghiP	6×10^{-2}	IRIS	7.10×10^{-8}	1.58×10^{-7}
PCBz	8×10^{-4}	IRIS	1.55×10^{-10}	NA
HCBz	8×10^{-4}	IRIS	2.52×10^{-10}	2.70×10^{-10}
Lindane (γ-HCH)	3×10^{-4}	IRIS	2.71×10^{-9}	NA
Heptachlor	5×10^{-4}	IRIS	6.58×10^{-10}	2.40×10^{-10}
Heptachlor epoxide	1.3×10^{-5}	IRIS	1.08×10^{-9}	NA
Chlorpyrifos	3×10^{-3}	IRIS	7.99×10^{-9}	2.18×10^{-10}
Chlordane	5×10^{-4}	IRIS	1.18×10^{-8}	NA
Dieldrin	5×10^{-5}	IRIS	3.96×10^{-9}	NA
Endosulfane	06×10^{-3}	IRIS	3.85×10^{-9}	NA
p,p´-DDD	2×10^{-3}	IRIS	3.77×10^{-9}	NA
Methoxychlor	5×10^{-3}	IRIS	1.65×10^{-9}	NA
Mirex	2×10^{-4}	IRIS	3.11×10^{-10}	NA

Table 27: OSFs given by EPA and CDI (carcinogenic) for mussels collected from Abu Qir Bay.

Analyte	OSF	Data origin	CDI *Mactra corallina*	CDI *Tapes decussata*
As	1.5	IRIS	6.79×10^{-6}	6.33×10^{-6}
PCBs (high risk)	2	IRIS	5.21×10^{-8}	7.06×10^{-9}
PCBs (low risk)	0.4	IRIS	5.21×10^{-8}	7.06×10^{-9}
PCBs (lowest risk)	0.07	IRIS	5.21×10^{-8}	7.06×10^{-9}
BaA	0.73	USEPA, 1993	9.03×10^{-8}	2.12×10^{-7}
Chy	0.0073	USEPA, 1993	8.41×10^{-8}	2.40×10^{-7}
BbF	0.73	USEPA, 1993	9.99×10^{-8}	2.53×10^{-7}
BkF	0.073	USEPA, 1993	6.02×10^{-8}	1.55×10^{-7}
BaP	7.3	IRIS	8.76×10^{-8}	2.10×10^{-7}
InP	0.73	USEPA, 1993	8.83×10^{-8}	2.03×10^{-7}
DibA	7.3	USEPA, 1993	5.36×10^{-8}	1.02×10^{-7}
HCBz	1.6	IRIS	2.62×10^{-10}	2.82×10^{-10}
α-HCH	6.3	IRIS	2.05×10^{-9}	NA
Lindane (γ-HCH)	1.3	HEAST	2.82×10^{-9}	NA
Heptachlor	4.5	IRIS	6.87×10^{-10}	2.51×10^{-10}
Heptachlor epoxide	9.1	IRIS	1.13×10^{-9}	NA
Chlordane	0.35	IRIS	1.23×10^{-8}	NA
Dieldrin	16	IRIS	4.13×10^{-9}	NA
p,p´-DDD	0.24	IRIS	3.93×10^{-9}	NA
pp´-DDE	0.34	IRIS	7.21×10^{-9}	NA
Mirex	1.8	IRIS	3.24×10^{-10}	NA

HEAST: Health assessment summary tables (http://rais.ornl.gov/cgi-bin/tox/TOX_select?select=nrad).
IRIS: Integrated risk information system (www.epa.gov/iris)
NA: not available

The calculated HQs for all of the investigated pollutants in both species are much lower than 0.1 indicating no probability of adverse noncarcinogenic human health effects through the mussel consumption. At the same time, all the calculated cancer risk values for the investigated organic pollutants were lower than the 10^{-6} risk level set by the USEPA. It was only As, which showed a cancer risk value between 10^{-4} and 10^{-6} (marked with bold font), and though it could be regarded as a contaminant of potential concern and that it may pose carcinogenic health effects. Finally, it can be concluded that it is safe to ingest mussels obtained from Abu Qir Bay at the used ingestion rate and that no health effects (carcinogenic and noncarcinogenic) are expected to occur from this exposure route.

Table 28: Calculated HQs and cancer risks in the performed human health risk assessment in Abu Qir Bay.

Analyte	*Mactra corallina*		*Tapes decussata*	
	HQ	**Cancer risk**	**HQ**	**Cancer risk**
As	2.20×10^{-2}	**1.02×10^{-5}**	2.02×10^{-2}	9.49×10^{-6}
Cd	2.00×10^{-3}	NA	1.22×10^{-3}	NA
Cr	5.20×10^{-6}	NA	1.23×10^{-6}	NA
Cu	2.10×10^{-4}	NA	1.75×10^{-4}	NA
Hg	2.3×10^{-2}	NA	1.78×10^{-2}	NA
Mn	7.71×10^{-4}	NA	4.41×10^{-5}	NA
Pb	1.78×10^{-3}	NA	1.39×10^{-3}	NA
Se	5.50×10^{-4}	NA	4.88×10^{-4}	NA
Zn	1.50×10^{-4}	NA	1.58×10^{-4}	NA
PCBs (high risk)	4.99×10^{-8}	1.01×10^{-7}	6.77×10^{-9}	1.41×10^{-8}
PCBs (low risk)	4.99×10^{-8}	2.08×10^{-8}	6.77×10^{-9}	2.82×10^{-9}
PCBs (lowest risk)	4.99×10^{-8}	3.65×10^{-9}	6.77×10^{-9}	4.94×10^{-10}
Nap	2.40×10^{-6}	NA	1.64×10^{-6}	NA
Ace	6.66×10^{-7}	NA	6.97×10^{-7}	NA
Flr	1.41×10^{-5}	NA	2.27×10^{-5}	NA
Phn	2.85×10^{-7}	NA	6.44×10^{-7}	NA
Ant	1.87×10^{-7}	NA	3.86×10^{-7}	NA
Fla	3.21×10^{-5}	NA	7.88×10^{-5}	NA
Pyr	3.85×10^{-6}	NA	9.81×10^{-6}	NA
BaA	NA	6.59×10^{-8}	NA	1.55×10^{-7}
Chy	NA	6.14×10^{-10}	NA	1.75×10^{-9}
BbF	NA	7.29×10^{-8}	NA	1.85×10^{-7}
BkF	NA	4.39×10^{-9}	NA	1.13×10^{-8}
BaP	NA	6.39×10^{-7}	NA	1.53×10^{-6}
InP	NA	6.45×10^{-8}	NA	1.48×10^{-7}
DibA	NA	3.91×10^{-7}	NA	7.46×10^{-7}
BghiP	1.18×10^{-6}	NA	2.63×10^{-6}	NA
PCBz	1.94×10^{-7}	NA	ND	NA
HCBz	3.14×10^{-7}	4.20×10^{-10}	3.38×10^{-7}	4.51×10^{-10}
α-HCH		1.29×10^{-8}	NA	ND
Lindane (γ-HCH)	9.02×10^{-6}	3.67×10^{-9}	ND	ND
Heptachlor	1.32×10^{-6}	3.09×10^{-9}	4.81×10^{-7}	1.13×10^{-9}
Heptachlor epoxide	8.31×10^{-5}	1.02×10^{-8}	ND	ND

NA: not available ND: not detected

Table 28: Continued.

Analyte	*Mactra corallina*		*Tapes decussata*	
	HQ	**Cancer risk**	**HQ**	**Cancer risk**
Chlorpyrifos	2.66×10^{-6}	NA	7.27×10^{-8}	NA
Chlordane	2.35×10^{-5}	4.29×10^{-9}	ND	ND
Dieldrin	7.92×10^{-5}	6.60×10^{-8}	ND	ND
Endosulfane	6.41×10^{-7}	NA	ND	NA
p,p´DDD	1.89×10^{-6}	9.44×10^{-10}	4.23×10^{-7}	2.12×10^{-7}
p,p´DDE	NA	2.45×10^{-9}	NA	7.45×10^{-9}
Methoxychlor	3.29×10^{-7}	NA	ND	NA
Mirex	1.55×10^{-6}	5.83×10^{-10}	ND	ND

4.2.5. HHRA of other food items in the Egyptian normal diet compared to the bivalves

Other food items normally found in the Egyptian daily diet were investigated in the present study in comparison to the results obtained from the HHRA of the mussels. The aim was to compare the adverse health effects (if found) caused from the mussel consumption with the health effects which could possibly occur from the consumption of other food items. Concentrations of pollutants in other food items were obtained from literature. The problem was either the scarcity of the available data on contaminants concentrations (especially organic pollutants) and/or that the available data were mostly more than 15 years old. So, only recent data were used. For fish, the maximum reported concentration of each pollutant in each species was collected and the average of these concentrations was calculated and used as the input data in the risk assessment. Ingestion rate for each type of food was obtained from Saleh et al. (1998) and Loutfy et al. (2006). Results of calculated HQ and cancer risks for the different food items are shown in **Table 29**. Not all types of Egyptian food could be covered due to the scarcity of available data. However, it can be seen that some of the Egyptian food items can pose either carcinogenic or noncarcinogenic human health effects. For instance, Hg and Se detected in fish samples catched along Alexandria Coast were found to cause noncarcinogenic health effects if ingested. At the same time, concentrations of PAHs (BbF, BaP, InP, DibA and the sum of the carcinogenic PAHs) detected in fish species in Alexandria in the study performed by EL-Deeb et al. (2007) were found to pose carcinogenic human health risks.

Human health effects (carcinogenic and noncarcinogenic) could also be expected from the consumption of fish sampled from Lake Qarun based on the detected concentrations of organochlorine pesticides in their tissues. In the study performed by Abou-Arab, (2001) regarding heavy metal content in Egyptian meat, it was found that Cd and Cu concentrations may pose adverse noncarcinogenic health effects. At the same time, adverse noncarcinogenic health effects could be expected from the ingestion of bread with respect to detected concentrations of Mn, Se and Zn (**Table 29**). As for vegetables and fruits, dieldrin was the only organochlorine pesticide that was found at concentrations possibly causing adverse carcinogenic health effects in onions, parsley, radish and strawberry and noncarcinogenic health effects in onions (**Table 29**).

Table 29: Calculated HQs and Cancer risk (CR) for different food items in Egypt.

Analyte	Concentration (mg/kg ww)	HQ	Cancer risk	Reference
Fish (Alexandria)				
Cd	0.05	0.03	NA	Ahdy,et al.2007, Abdallah and Abdallah, 2007
Cr	1.24	0.0004	NA	
Cu	1.35	0.018	NA	
Hg	0.24	**1.29**	NA	
Mn	0.749	0.003	NA	
Se	2.95	**0.32**	NA	
Zn	18	0.03	NA	
Nap	0.00890	0.0002	NA	EL-Deeb et al.2007
Ace	0.212	0.002	NA	
Phn	0.0522	9.37×10^{-5}	NA	
Ant	0.0313	5.62×10^{-5}	NA	
Pyr	0.00212	3.80×10^{-5}	NA	
BaA	0.0019		7.79×10^{-7}	
Chy	0.0144		5.90×10^{-6}	
BbF	0.036		**1.48×10^{-5}**	
BkF	0.145		5.94×10^{-6}	
BaP	0.195		**8.00×10^{-4}**	
InP	0.079		**3.24×10^{-5}**	
DibA	0.267		**1.10×10^{-3}**	
BghiP	0.301	1.86×10^{-5}	NA	
TPAHs			**4.10×10^{-4}**	
Fish from Nile River				
α-HCH	0.0018		6.37×10^{-6}	Mansour, 2004
Lindane (γ-HCH)	0.0011	0.002	8.39×10^{-7}	
Heptachlor	0.00163	0.002	4.12×10^{-6}	
Chlordane	0.00046	0.0005	9.04×10^{-9}	
p,p'-DDE	0.0168		3.21×10^{-6}	
Fish from Lake Qarun				
HCBz	0.0577	0.04	**5.18×10^{-5}**	Mansour, 2004
Lindane (γ-HCH)	0.094	**0.17**	**6.86×10^{-5}**	
Heptachlor	0.068	0.07	**1.72×10^{-4}**	
Heptachlor epoxide	0.0313	**1.30**	**1.60×10^{-4}**	
Dieldrin	0.027	**0.29**	**2.42×10^{-4}**	
p,p'-DDE	0.00033		6.30×10^{-8}	
p,p'-DDD	0.0233	0.006	3.14×10^{-6}	

Table 29: Continued.

Analyte	Concentration (mg/kg ww)	HQ	Cancer risk	Reference
Crustacea				
Cd	0.590	0.002	NA	Ahdy,et al.2007
Cr	1.20	2.96×10^{-6}	NA	
Cu	3.40	3.1×10^{-4}	NA	
Hg	0.170	6.29×10^{-3}	NA	
Se	3.90	2.90×10^{-3}	NA	
Pb	0.06	6.00×10^{-5}	NA	
Zn	24.0	3.00×10^{-4}	NA	
Meat				
Cd	0.776	**0.285**	NA	Abou-Arab, 2001
Cu	61.7	**0.566**	NA	
Mn	4.06	0.01	NA	
Pb	0.656	0.07	NA	
Zn	56.7	0.07	NA	
Bread				
Cr	1.95	3.60×10^{-3}	NA	Iskander and Davis, 1992
Mn	19.4	**0.384**	NA	
Se	0.393	**0.218**	NA	
Zn	23.2	**0.214**	NA	
Wheat flour				
Mn	45.0	6.79×10^{-3}	NA	Iskander and Davis, 1992
Zn	24.7	0.002	NA	
Vegetables (Spinach)				
HCBz	6.00	3×10^{-4}	4.3×10^{-7}	Mansour, 2004
Lindane (γ-HCH)	11.0	2×10^{-3}	6.3×10^{-7}	
Dieldrin	4.00	3×10^{-3}	2.8×10^{-6}	
Vegetables (Parsley)				
HCBz	1.0	8.6×10^{-5}	1.1×10^{-7}	Mansour, 2004
Lindane (γ-HCH)	34.0	8×10^{-3}	3.2×10^{-6}	
Dieldrin	14.0	1.9×10^{-2}	**1.6×10^{-5}**	
Vegetables (Onion)				
HCBz	9.0	2×10^{-3}	3.3×10^{-6}	Mansour, 2004
Lindane (γ-HCH)	18.0	1.4×10^{-2}	5.4×10^{-6}	
Dieldrin	103	**5×10^{-1}**	**3.8×10^{-4}**	

NA: not available

Table 29: Continued.

Analyte	Concentration (mg/kg ww)	HQ	Cancer risk	Reference
Vegetables (Radish)				
HCBz	1.0	3.4×10^{-5}	4.6×10^{-8}	Mansour, 2004
Lindane (γ-HCH)	8.0	7×10^{-4}	3.0×10^{-7}	
Dieldrin	22.0	1.2×10^{-2}	**1.0×10^{-5}**	
Vegetables (Lettuce)				
HCBz	9.0	3×10^{-4}	3.7×10^{-7}	Mansour, 2004
Lindane (γ-HCH)	11.0	9×10^{-4}	3.7×10^{-7}	
Dieldrin	1.0	5×10^{-4}	4.1×10^{-7}	
Fruits (Tomatoes)				
HCBz	9.0	1×10^{-3}	1.5×10^{-6}	Mansour, 2004
Lindane (γ-HCH)	3.0	2×10^{-4}	1.0×10^{-7}	
Dieldrin	ND	NA	NA	
Fruits (Strawberry)				
HCBz	29.0	2×10^{-4}	2.3×10^{-7}	Mansour, 2004
Lindane (γ-HCH)	3.0	2×10^{-4}	1.0×10^{-7}	
Dieldrin	220	$2 * 10^{-2}$	**1.7×10^{-5}**	

NA: not available

ND: not detected

Finally, it must be pointed out that the available data are not enough to build a complete image about the health effects expected to occur from the ingestion of all types of food in a single meal based on the detected organic and inorganic pollutants as data are not available for all the food items. But it can be concluded that other food items contain higher concentrations of metals and trace organic pollutants compared to the two bivalve species investigated in the present study, and thus higher risks of adverse health effects could be accompanied by the consumption of these food items.

5- Conclusions

Sediments are important hosts for trace metals and trace organic pollutants and as such should be included in environmental monitoring programs. The investigation of sediments in Abu Qir Bay revealed that the bay is enriched with trace metals, PAHs and organochlorine pesticides. PCBs were detected but in lower concentrations compared to the investigated organic pollutants. The spatial distribution of the different investigated pollutants showed that the bay is greatly influenced by the wastewaters discharged from AQD and the polluted water of Lake Edku discharged via Maadeya Outlet. The spatial distribution of the investigated pollutants was also found to be influenced by the physicochemical properties of the sediments (grain size and TOC content) and the circulation pattern of water in Abu Qir Bay, where pollutants were recorded in locations away from the major sources of pollution in the bay (AQD and Maadeya Outlet)

Due to the lack of time based data on the levels of the different pollutants in the bay sediments, it was not possible to postulate a specific time trend for the concentrations of the investigated pollutants. Trace metals concentrations showed a great variability when compared to the previous studies performed on sediments on Abu Qir bay, but in general, it was concluded that there were no extreme increase or decrease in the detected concentrations of trace metals in the present study when compared with literature. For the investigated organochlorine pesticides and PCBs, concentrations found in the present study were much lower than concentrations reported previously, which could possibly be related to the banning of the use of the organochlorine pesticides, not only in Egypt, but worldwide. Calculated ratios of DDT and its metabolites revealed that the DDTs detected in the bay sediments were aged, which could support the lower concentrations reported in the present study.

Few studies investigated the levels of PAHs in Abu Qir Bay sediments, but the concentrations found in the present work were within the same range as those reported in a recent study on the levels of PAHs in the bay sediments.

Monitoring of the environmental quality of coastal areas using marine organisms as bioindicators has been widely used worldwide in many monitoring programs. Mussels were preferentially selected because they are sedentary and have low level of enzymatic metabolic activities. Mussels can biaccumulate pollutants at high levels, even higher than the surrounding water or sediments. In the present study, it was found that *Mactra corallina* and *Tapes decussata* were successfully used as bioindicators of the environmental quality of Abu Qir Bay, and that they could be incorporated in the future in biomonitoring programs regarding the quality of Abu Qir Bay. Concentrations of most of the investigated pollutants (except organochlorine pesticides and some trace metals) were higher in the tissues of mussels especially *Mactra corallina*.

The SLERA conducted in Abu Qir Bay to study the possible hazard induced by different classes of contaminants in sediments highlighted two major problems: one related to the scarcity of information

available on the concentrations of different pollutants in sediments and marine organisms, and thus no integrated and updated database was available. The second problem was related to the effects and guidelines, as no SQGs were available to the region or even to the Mediterranean Sea. At the same time, on-site ecotoxicological data was not available. In spite of these limitations, the adopted approach in the present study highlighted which contaminants are of ecological concern and, thus, a further detailed investigation based on site specific studies and including different marine species from different trophic levels would be greatly required. Based on the above limitations and the results obtained from the present study, the following recommendations could be greatly helpful in the improvement and the future management of Abu Qir Bay:

- Like many countries in the Mediterranean region, there are no emission inventories of sources or release of organic and inorganic pollutants in the Egyptian environment, or any official data on stockpiles and disposal. In order to determine and control the sources of the observed contaminants of potential concern, intense localized sampling and analysis of effluents and runoff patterns would be needed.
- A detailed study on the transport, behaviour and fate of contaminants of potential concern should be indeed encouraged.
- As a way of decreasing the variability in the obtained concentrations of pollutants in the different mediums, methods of sampling and analysis from Abu Qir Bay should be unified between different laboratories in different institution and even within the same institution.
- Selection of specific bioindicators that can be used to monitor the quality of the bay.
- A detailed level ecological risk assessment should be conducted for the determined contaminants of potential concern, including ecotoxicological tests conducted both on each chemical pollutant of concern and as a mixture.
- Development of environmental quality criteria for Abu Qir Bay based on the detailed risk assessment.
- Establishment of few routine monitoring sites, especially near the major sources of pollution in the bay.
- Prevention, reduction and control of pollution caused by discharges from land-based activities and shipping activities.
- The capabilities of national institutions to carry out marine pollution monitoring and research should be supported, developed and when necessary established to formulate and apply pollution control and abatement measures.
- Continuous evaluation of short and long term impacts of major pollutants on the coastal sediments of Abu Qir Bay.

6- Summary

In an attempt to evaluate the environmental quality of Abu Qir Bay, an important highly productive area in Alexandria, Egypt, an environmental risk assessment was performed; including a screening level ecological risk assessment (SLERA) and a human health risk assessment (HHRA). The aim of this risk assessment was to determine which classes of chemical pollutants could possibly pose adverse ecological effects to benthic species and to determine whether hot spots exist or not (SLERA). At the same time, this work tried to elucidate the possibility of occurrence of adverse health effects for local residents of Abu Qir Bay as a result of the consumption of mussels (HHRA).

To fulfil our goals, 30 surfacial sediment samples were collected from different locations covering the region from the harbour area till the Maadeya Outlet. This region was selected because it receives the majority of the industrial, agricultural and urban effluents (land-based activities), and thus expected to be more contaminated than the rest of the bay regions. At the same time, two mussel species were collected from the bay: *Mactra corallina* and *Tapes decussata*. Two species were collected because none of them covered the whole investigated region of Abu Qir Bay. Especially that the bivalve species were collected from the same sampling sites as the sediment samples.

Sediment samples were analyzed for metals (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, V and Zn), PAHs (16 EPA priority PAHs), PCBs (PCB 28, 52, 70, 101, 118, 153, 138, 126, 156, 180 and 169), PCBz, HCBz, chlorpyrifos (organophosphate pesticide) and organochlorine pesticides (α-HCH, β-HCH, γ-HCH, δ-HCH, heptachlor, cis-heptachlor epoxide, trans-heptachlor epoxide, aldrin, dieldrin, cis-chlordane, trans-chlordane, α-endosulfane, β-endosulfane, o,p´-DDE, o,p´-DDD, o,p´-DDT, p,p´-DDE, p,p´-DDD, p,p´-DDT, methoxychlor and mirex). These pollutants were selected because either they were previously detected in the bay sediments or because of the ecotoxicological risk associated with the exposure to these pollutants. Bivalve samples were analyzed for the same trace organic pollutants but for 8 metals (As, Cd, Cr, Cu, Hg, Mn, Pb, Se and Zn). These selected metals are considered the most toxic for bivalve species (from literature) and for the human health.

The investigated sediments were dominated by the sand fraction, except in the nearshore stations that were dominated by the fine fraction (silt + clay), where sediments are possibly affected by detrital and organic particles discharged by the land-based activities. For all the investigated classes of pollutants (except for PAHs), higher concentrations were always observed in sediments in front of the Abu Qir Drain, the Fertilizer Company, the Maadeya Outlet and in some cases (as Pb and Cr) in front of the Electric Power Plant. Concentrations were found to decrease generally in the offshore direction except for the nearshore-offshore profile in front of the Petroleum Company, where relatively high concentrations of most of the investigated pollutants were observed in station 14, reflecting the role played by the water circulation pattern in distributing pollutants in sites away from the major sources of pollution inputs (Abu Qir Drain, the Fertilizer Company and the Maadeya Outlet).

Concentrations of total Ni, Co, Cr, Pb and V showed close pattern of spatial distribution in the bay sediments. Cu and Zn concentrations were much higher in front of the Abu Qir Drain and the Fertilizer Company. Hg and Sn total concentrations were higher in front of the Maadeya Outlet and in the offshore direction too reflecting the influence of the discharged agricultural wastes and shipping activities respectively. Concentrations of all metals were lower in the western part of the bay. Most of the investigated metals (except Se and Sn) showed significant positive correlation with clay content and the Fe %, which may indicate that metals could have entered the bay either adsorbed on Fe oxyhydroxides and/or scavenged by the Fe oxyhydroxides when they entered the bay waters.

Results obtained from the sequential extraction procedure revealed that the majority of Ni and Co were incorporated in the residual fraction of the sediments, thus chemically inactive. Although the residual fraction of Fe, Cr, Mn and Zn showed the highest percentage compared to the other 4 fractions, the sum of the first four non-residual fractions were higher than the residual fraction of each element, especially the reducible fraction, which showed a significant portion of the total metal concentration in Fe and Cr. At the same time, the reducible fraction showed the highest concentrations of Pb and V. The oxidizable fraction of Cu was found to be the dominant fraction which may indicate the association of Cu with organic matter in the bay sediments. High significant positive correlation was observed between concentrations of the reducible Fe and concentrations of the labile fractions of metals (F1 + F2 + F3), which confirm the strong association between metals and the reactive Fe in the bay sediments. The anthropogenic influence on the investigated trace metals concentrations was identified in most of the investigated sediment samples, especially for Se, Cd, Hg and Pb. These elements were highly enriched in relation to Al, which was used as the normalizer.

Concentrations of total metals were generally higher in the *Mactra corallina* than in *Tapes decussata*. Relatively higher concentrations of metals were generally observed in front of the Maadeya Outlet. Mn, Zn and Cu showed the highest concentrations of metals in both species. Concentrations of As, Cd, Cu, Se, Hg and Zn in some samples were higher than their corresponding sediment concentrations, indicating that these elements are possibly present in a more bioavailable form. Significant positive correlation was observed between concentrations of As, Cu, Se and Zn in sediments and tissues of *Mactra corallina*. The labile fraction of metals in sediments is expected to be the fraction available for uptake and accumulation by marine organisms, and thus a strong relation could be expected between the labile fraction of metals and metal concentrations in marine organisms. In the present study, high significant positive correlation was observed between concentrations of Mn, Zn, Pb and to a lesser extent Cu in the *Mactra coralline* and the labile fraction of these metals in the bay sediments. Weak or no correlation was observed between concentrations of total metals in sediments and tissues of *Tapes decussata*. This could arise from the fact that concentrations of total metals in the sediments corresponding to the sampling sites of *Tapes decussata* were low, possibly lower than the threshold level that mussels can regulate the accumulation of these metals from the sediments.

Detected concentrations of metals in sediments were compared with concentrations worldwide and with previous concentrations reported for Abu Qir Bay. In general, none of the metals showed extreme concentration when compared worldwide. As for the mussel samples, higher concentrations of As, Hg and Pb were observed in the present study when compared worldwide and with previous studies performed along the Alexandrian Coast including Abu Qir Bay. It must be pointed out that different species were investigated in the previous studies and no data are available for concentrations of different pollutants in tissues of *Tapes decussata*.

Low concentrations of PCBs were observed in sediments of Abu Qir Bay when compared with concentrations recorded in other coastal sediments worldwide or previously in Abu Qir Bay. Sediments were dominated by the tetra, penta and hexa chlorinated biphenyls. Coplanar PCBs were either detected in low concentrations or below the limit of detection in most of the investigated sediment samples except in front of the Abu Qir Drain and the Fertilizer Company, where the highest PCB concentrations were recorded. Concentrations of PCBs in the mussels especially *Mactra corallina* were higher than concentrations recorded in their corresponding sediment samples. Like in sediments, the mussel tissues were dominated with the higher chlorinated chlorobiphenyls

Relatively high concentrations of DDTs, chlordanes, chlorpyrifos and HCHs were recorded in sediments of Abu Qir Bay. Other pesticides (dieldrin, aldrin, endosulfane, heptachlor and its epoxides) were detected in the bay sediments but at lower concentrations. Sediments were dominated by the metabolites of DDT (DDD and DDE) indicating that the detected DDTs in the bay sediments are aged and not recently introduced into the bay. At the same time, DDD concentrations were higher than DDE indicating possibly the preferred reductive dechlorination pathway of DDT in the bay sediments. In the mussel species, p,p´-DDE was the dominant metabolite, which could possibly be related to a metabolic pathway, depuration mechanism or a certain preferable uptake by the mussel species from the surrounding medium

Chlordanes were recorded both in sediments and the mussel samples precisely *Mactra corallina*. trans-Chlordane concentrations were higher than the cis isomer in sediments and the mussel tissues, possibly due to the normal composition of the technical chlordane. Concentrations of dieldrin the sediment samples were higher than aldrin possibly due to the metabolism of aldrin in the bay sediments, which is converted to dieldrin by epoxidation. Concentrations of α-endosulfane were higher than β-endosulfane in sediments of Abu Qir Bay.

HCH concentrations were generally lower than DDTs and chlordanes in sediments and mussel tissues of Abu Qir Bay. HCHs were dominated by the γ-isomer, followed by the α-isomer in sediments and mussels. Calculated ratios for both isomers in the sediment samples revealed that lindane rather than the HCH technical mixture was used in the region.

Relatively high concentrations of chlorpyrifos were observed in the sediments and mussels, which could possibly be due to the intensive application of organophosphate pesticides after banning or restricting the use of the organochlorine pesticides.

Detected concentrations of organochlorine pesticides (DDTs, chlordane and HCHs) in sediments of Abu Qir Bay were generally high compared to concentrations worldwide except in some severely contaminated locations such as sediments of San Francisco Bay, California, and Saronikos Gulf, Greece, and some severely contaminated sites along the Mediterranean Sea.

In contrast to all the investigate pollutants, the highest concentration of PAHs in sediments and mussels was observed in the western part of the bay (station 27) possibly affected by the shipping activities. Sediments and mussels were dominated by the higher molecular weight PAHs (4, 5 and 6-rings PAHs). Weak correlation was observed between sediment concentrations of PAHs and TOC %, which could possibly be related to the detected concentrations of PAHs in the sediments, which were lower than 2000 µg/kg dw in all the sediment samples except for only one sample and/or the absence of equilibrium, which means that fresh inputs of PAHs are still introduced to the bay sediments. Good correlation was observed between PAHs concentrations in sediments and mussels. Close pattern of PAHs was observed in mussels and sediments when the sediment PAH concentrations were higher than 200 µg/kg dw (stations 4, 8 and 19). In other locations there were some differences between detected PAHs in the mussels and their corresponding sediment sample, which could be attributed to the metabolic pathway in the mussels and /or different routes of PAH uptake from the bay (sediments, contaminated food or water uptake).

It was found that the pyrogenic origin dominated over the petrogenic origin in most of the investigated sediment samples and mussels. At the same time, it was found that combustion of wood, coal and grass was the major pyrogenic origin in most of the investigated samples. Some exceptions were observed at station 27, which showed that petroleum combustion was the dominant source possibly from the shipping exhaust systems. In other stations such as station 20, a mixed pattern of pyrogenic and petrogenic origin was observed and thus the ratios based on the parent PAHs couldn't determine exactly which source dominates.

Detected concentrations of PAHs in the bay sediments were generally lower than concentrations recorded in other contaminated coastal sediments in the Mediterranean Sea and lower than concentrations recorded along the Alexandrian Coast. At the same time, relatively high concentrations of PAHs were observed in the mussels compared to other mussel species worldwide.

The output of the SLERA (based on the consensus approach) revealed that Hg, Zn, Cd, DDD, DDTs, dieldrin, chlordane, lindane, heptachlor (all had PEC HQ > 1), Pb, p,p´-DDE and p,p´-DDT (TEC HQ > 1 > PEC HQ) could be considered as contaminants of potential concern and that adverse ecological effects are expected to occur for the benthic species when exposed to the bay sediments. At the same

time, endosulfane, chlorpyrifos, heptachlor epoxides, which were evaluated based on the available screening benchmark concentration could also be regarded as contaminants of potential concern and could be included in a more detailed risk assessment with site specific studies. Concentrations of aldrin and HCBz were lower than the PEC, but no TEC was available for both organic contaminants, and thus could also be included in a more detailed study. On the other hand, As, Cr, Cu, PCBs, PCBz, methoxychlor, α-HCH and PAHs, could be safely screened out and not included in a further detailed study as rare adverse ecological effects are expected from the exposure to these pollutants in the bay sediments.

In the mussels, As, Cd, Cu, Hg and Zn concentrations were higher than the toxicity reference values aiming at the protection of 95 % of the benthic species and thus could possibly be a sign of the probability of occurrence of effects. On the other hand, tissue concentrations of all the investigated pollutants in this risk assessment were lower than all toxicity data available for *Mytilus edulis* and *Mytilus galloprovincialis*.

In the HHRA, it was concluded that except for As, no adverse threshold or nonthreshold health effects are expected to occur from the ingestion of both mussel species at the available ingestion rate and thus both species can be ingested safely. In the case of As, the calculated cancer risk in *Mactra corallina* was between the 10^{-6} and 10^{-4} cancer level set by the USEPA as an acceptable level.

Compared to other items of the normal Egyptian diet, carcinogenic and noncarcinogenic health effects could be more expected from the ingestion of other types of food such as fish, bread, meat and vegetables.

Zusammenfassung

Um die Umweltqualität der Abu Qir Bucht, einem bedeutendem Gebiet in Alexandria, Ägypten einzuschätzen, wurde eine Umweltrisikobewertung (**E**nvironmental **Ri**sk **A**ssesment) durchgeführt. Diese beinhaltete eine ökologische Risikobewertung (**S**creening **L**evel **E**cological **R**isk **A**ssessment) und ein **H**uman **H**ealth **R**isk **A**ssessment. Das Ziel der Risikoeinschätzung war es, mögliche Hot Spots aufzudecken und zu ermitteln, welche chemische Verunreinigungen möglicherweise nachteilige ökologische Effekte für benthische Arten verursachen. Weiterhin wird die Frage geklärt, ob mögliche Gesundheitsschäden der Bewohner der Abu Qir Bucht durch den Verzehr von Muscheln auftreten können.

Für die Untersuchungen wurden 30 Sedimentproben an verschiedenen Punkten zwischen Hafen und Maadeya-Abfluss erfasst. Diese Region wurde ausgewählt, da hier der Großteil der industriellen, landwirtschaftlichen und häuslichen Abwässer eingeleitet und somit eine besonders hohe Kontamination erwartet wird. Im gleichen Zeitraum wurden Proben zwei verschiedener Muschelarten (*Mactra corallina* und *Tapes decussata*) gesammelt. Es wurden zwei verschiedene Muschelarten gewählt, da keine von beiden im gesamten Untersuchungsbereich der Abu Qir Bucht vorkommt, aber die Probenpunkte der Muscheln mit denen der Sedimentproben übereinstimmen sollten.

Die Sedimentproben wurden auf Metalle (Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sn, V und Zn), PAKs (16 nach EPA), PCBs (PCB 28, 52, 70, 101, 118, 153, 138, 126, 156, 180 and 169), PCBz, HCBz Chlorpyrifos (Organophosphorpestizid) und Organochlorpestizide (α-HCH, β-HCH, γ-HCH, δ-HCH, Heptachlor, cis-Heptachlorepoxid, trans-Heptachlorepoxid, Aldrin, Dieldrin, cis-Chlordan, trans-Chlordan, α-Endosulfan, β-Endosulfan, o,p´-DDE, o,p´-DDD, o,p´-DDT, p,p´-DDE, p,p´-DDD, p,p´-DDT, Methoxychlor und Mirex) untersucht. Diese Schadstoffe wurden ausgewählt, da sie einerseits für das Untersuchungsgebiet bereits in der Literatur beschrieben worden sind und andererseits wegen ihrer möglichen ökotoxikologischen Effekte auf benthische Organismen. Die Muscheln wurden auf dieselben organischen Parameter untersucht, jedoch nur auf 8 ausgewählte Metalle (As, Cd, Cr, Cu, Hg, Mn, Pb, Se and Zn). Diese sind laut Literaturangaben sowohl für den Menschen als auch für die Muscheln besonders toxisch.

In den untersuchten Sedimenten dominiert die Sandfraktion. Nur die ufernahen Sedimente zeichnen sich durch einen hohen Anteil an der feinkörnigen Fraktion (Schluff und Ton) aus, verursacht durch vom Land eingetragenen Detritus und organische Partikel. Alle untersuchten Schadstoffe (außer PAKs) wurden in erhöhten Konzentrationen im Küstenbereich des Abu Qir Abflusses, der Düngemittelfabrik, des Maadeya-Abflusses und in einigen Fällen (hier nur Pb und Cr) vor dem Elektrizitätswerk beobachtet. Die Konzentrationen nahmen in Richtung offene See ab. Eine Ausnahme ist der Küstenbereich vor einem Petroleumbetrieb, wo fast alle untersuchten Schadstoffe in

hohen Konzentrationen (Station 14) beobachtet wurden. Dies zeigt, welche bedeutende Rolle die Wasserzirkulation bei der Verteilung von Schadstoffen spielt.

Die Konzentrationen von Ni, Co, Cr, Pb und V zeigten eine räumliche Verteilung in den Sedimenten der Bucht. Erhöhte Konzentrationen von Cu und Zn wurden im Gebiet des Abu Qir Abflusses und der Düngemittelfabrik gefunden. Hg und Sn zeigten erhöhte Konzentrationen am Maadeya-Abfluss und Richtung offene See, verursacht durch landwirtschaftliche Abwässer und Schiffsverkehr. Alle Metalle zeigten geringere Konzentrationen im westlichen Teil der untersuchten Bucht. Fast alle untersuchten Metalle (außer Se und Sn) zeigten signifikant positive Korrelationen sowohl mit dem Ton- als auch mit dem Eisengehalt. Dies zeigt möglicherweise, dass die Metalle durch Adsorption und/oder Einfangen an Eisenoxyhydroxiden in die Bucht gelangten.

Die sequentielle Extraktion zeigte, dass Ni und Co in der Residualfraktion der Sedimente vorkommen und somit chemisch inaktiv vorliegen. Obwohl die Residualfraktion der Elemente Fe, Cr, Mn und Zn verglichen mit jeder einzelnen Fraktion der anderen vier Fraktionen den höchsten Anteil aufweist, ist für diese Elemente die Summe der vier mobilen Fraktionen größer als die Residualfraktion. Besonders Fe und Cr machen einen hohen Anteil in der reduzierbaren Fraktion aus. Den höchsten Anteil in dieser Fraktion zeigen Pb und V. Cu zeigt die höchsten Anteile in der oxidierbaren Fraktion, was auf seine Vergesellschaftung mit organischer Materie zurückzuführen ist. Eine hohe positive Korrelation zeigen die Konzentrationen des reduzierten Eisens und die Konzentrationen der Metalle in den schwächer gebundenen Fraktionen (Fraktionen 1 bis 3). Dies weist auf die starke Assoziation zwischen Spurenmetallen und dem reaktivem Eisen in den Sedimenten hin. Der anthropogene Einfluss der untersuchten Spurenmetalle konnte in den Sedimenten nachgewiesen werden, besonders deutlich für Se, Cd, Hg und Pb. Diese waren in Bezug auf Aluminium, welches zur Normalisierung verwendet wurde, stark angereichert.

Die gefundenen Metallkonzentrationen waren generell in *Mactra corallina* höher als in *Tapes decussata*. Am Maadeya-Abfluss wurden jeweils die höchsten Metallkonzentrationen gemessen. Mn, Zn und Cu waren in beiden Muschelarten mit den höchsten Konzentrationen zu finden. As, Cd, Cu, Se, Hg und Zn zeigten in einigen Muschelproben höhere Konzentrationen als die korrespondierenden Sedimente der gleichen Probennahmepunkte, was darauf hindeutet, dass sie in einer leicht bioverfügbaren Form vorliegen. Hohe positive Korrelationen wurden zwischen den Konzentrationen von As, Cu, Se und Zn der Sedimente und *Mactra corallina* gefunden. Die Metalle der labilen Fraktion in den Sedimenten sind leicht verfügbar und werden so von den marinen Organismen aufgenommen und akkumuliert, sodass eine enge Korrelation zwischen der labilen Fraktion der Sedimente und der Metallkonzentration in den marinen Organismen erwartet wird. In dieser Arbeit wurden hohe positive Korrelationen zwischen den Konzentrationen von Mn, Zn, Pb und (etwas weniger ausgeprägt) Cu in *Mactra corallina* und den Konzentrationen dieser Metalle in der labilen Fraktion der Sedimente festgestellt. Keine oder nur schwache Korrelationen zeigten die Metallkonzentrationen zwischen den Sedimenten und *Tapes decussata* der gleichen Probennahmepunkte. Dies kann darauf

zurückzuführen sein, dass die Metallkonzentrationen in den korrespondierenden Sedimentproben gering sind. Diese geringen Metallkonzentrationen, die im Bereich der Hintergrundkonzentration der durchschnittlichen Schelfsedimente liegen, weisen darauf hin, dass die Metalle aus den Sedimenten für *Tapes decussata* nicht bioverfügbar sind und eine Akkumulation hauptsächlich aus Wasser und Nahrung erfolgt.

Die gefundenen Metallkonzentrationen in den Sedimenten wurden mit weltweit gemessenen Konzentrationen in Küstensedimenten und bereits im Untersuchungsgebiet gemessenen Werten verglichen. Keines der Metalle zeigt extreme Gehalte.

In den Muschelproben wurden im Vergleich zu weltweit gemessenen Gehalten in marinen Muscheln hohe Konzentrationen an As, Hg und Pb gefunden. Frühere Studien an der Küste von Alexandria (inbegriffen der Abu Qir Bucht) zeigten geringere Werte, allerdings wurden hier andere Arten untersucht. Für *Tapes decussata* liegen in der Literatur keine Vergleichswerte für Schadstoffe vor.

In den Sedimenten der Abu Qir Bucht wurden sowohl im Vergleich mit älteren Literaturdaten zu Sedimenten der Bucht sowie weltweiten Küstengebieten geringe Konzentrationen an PCBs nachgewiesen. Am höchsten sind die Sedimente mit tetra-, penta- und hexachlorierten Biphenylen belastet. Koplanare PCBs wurden in den meisten Sedimentproben nur in geringen Konzentrationen nachgewiesen oder die Konzentration lag unterhalb der Bestimmungsgrenze. Ausgenommen davon sind die Sedimentproben im Bereich der Abu Qir-Abflussrinne und der Düngemittelfabrik, in denen die höchsten PCB-Konzetrationen bestimmt werden konnten. Die PCB-Gehalte in den Muscheln, insbesondere der *Mactra corallina*, waren höher als in den korrespondierenden Sedimentproben. Wie in den Sedimentproben wurden auch in den Muscheln höher chlorierte Chlorbiphenyle nachgewiesen.

In den Sedimenten der Abu Qir Bucht wurden relativ hohe Konzentrationen an DDT, Chlordan, Chlorpyrifos und HCHs erfasst. Andere Pestizide, wie Dieldrin, Aldrin, Endosulfan, Heptachlor und dessen Epoxyde wurden in geringer Konzentration nachgewiesen. Dominierend dabei waren die Metaboliten von DDT (DDD und DDE), was ein Indikator für ein fortgeschrittenes Alter der DDT-Kontamination ist und somit nicht aus jüngster Vergangenheit stammen kann. Zudem war die Konzentration an DDD höher als die von DDE, was eine reduktive Dechlorierung von DDT im Sediment nahe legt. In den Muschelproben war p,p´-DDE der dominierende Metabolit. Der Grund dafür kann sowohl Metabolismus in den Muscheln als auch die selektive Aufnahme durch die Muschel aus dem umgebenden Medium sein.

Chlordan wurde sowohl in den Sedimenten als auch in den Muschelproben von *Mactra corallina* nachgewiesen. Die Konzentrationen von *trans*-Chlordan waren in den Sedimenten und in den Muscheln höher als die des *cis*-Isomers, was möglicherweise an der Zusammensetzung des technischen Chlordans liegt. Die Konzentrationen von Dieldrin waren in den Sedimentproben höher als die Konzentrationen von Aldrin, was durch die Metabolisierung von Aldrin zu Dieldrin durch

Epoxidierung begründet werden kann. In den Sedimentproben der Abu Qir Bucht waren die Konzentrationen von α-Endosulfan höher als die Konzentrationen von β-Endosulfan.

Die Konzentrationen an HCHs waren in den Sediment- und Muschelproben der Abu Qir Bucht im Allgemeinen geringer als die Konzentrationen an DDT und Chlordanen. Das γ-Isomer (Lindan) von HCH dominiert in den untersuchten Proben, gefolgt durch das α-Isomer. Das ermittelte Verhältnis beider Isomere in den Sedimentproben zeigt, dass Lindan häufiger in der Region zum Einsatz kommt als technisches HCH.

In den Sediment- und Muschelproben wurden relativ hohe Konzentrationen an Chlorpyrifos nachgewiesen, was den Schluss nahe legt, dass nach dem Verbot bzw. der Einschränkung von organochlorierten Pestiziden weiterhin Organophosphate als Pestizide eingesetzt wurden.

Die ermittelten Konzentrationen von Organochlorpestiziden in den Sedimenten der Bucht von Abu Qir waren im Vergleich zu den weltweit ermittelten Konzentrationen im Allgemeinen hoch, abgesehen von einigen wenigen kontaminierten Sedimenten wie die der Bucht von San Francisco, im Golf von Saronikus in Griechenland oder einigen kontaminierten Orten entlang des Mittelmeeres.

Im Gegensatz zu allen anderen untersuchten Schadstoffen war die höchste Konzentration an PAKs in den Sedimenten und Muscheln im westlichen Teil der Bucht (Station 27) zu beobachten, was möglicherweise auf Schifffahrtsaktivitäten zurückzuführen ist. Der Hauptteil an Schadstoffen in den Sedimenten und Muscheln bestand vor allem aus den PAKs mit höheren molekularen Gewichten, wie denjenigen mit 4, 5 und 6 aromatischen Ringen. Nur eine schwache Korrelation fand sich zwischen der ermittelten Konzentration der PAKs in den Sedimenten und dem TOC. Die möglichen Gründe hierfür liegen zum einen an den in allen Sedimenten gefundenen niedrigen Konzentrationen an PAKs (< als 2000 µg/kg TM - nur eine Probe war höher). Zum anderen hat sich möglicherweise noch kein Gleichgewicht zwischen dem TOC und den eingetragenen PAKs eingestellt, da vermutlich weiterhin PAKs in die Bucht eingetragen werden. Zwischen den PAKs in den Sedimenten und in den Muscheln fand sich eine hohe Korrelation. Sehr ähnliche PAK-Muster traten in beiden Probenarten (Sediment und Muschel) an gleichen Probennahmepunkten auf, aber nur wenn die Konzentration an PAKs höher lag als 200 µg/kg TM (Stationen 4, 8 und 19). An anderen Probennahmepunkten wurden Unterschiede zwischen den gemessenen PAKs in den Muschel- und den korrespondierenden Sedimentproben beobachtet. Dies kann auf den Stoffwechselweg der PAKs in den Muscheln und/oder den unterschiedlichen Wegen der Aufnahme der PAKs aus der Bucht (Sedimente, kontaminierte Nahrung oder Aufnahme über das Wasser) zurückzuführen sein.

In den meisten der untersuchten Sedimente und Muscheln überwiegt die pyrogene Eintragsquelle gegenüber der petrogenen. Die Verbrennung von Holz, Kohle und Gras sind die hauptsächlichen pyrogenen Quellen in den meisten der untersuchten Proben. Ausnahme ist Station 27, bei der die Verbrennung von Öl als wesentliche Eintragsquelle dominiert. Dieser Umstand wird möglicherweise

durch Schiffsabgase hervorgerufen. An anderen Probennahmepunkten wie der Station 20 wurde ein für PAK-Muster erhalten, dass für einen gemischten Eintrag aus pyrogenen und petrogenen Quellen spricht.

Die gefundenen Konzentrationen der PAKs in den Sedimenten aus der Bucht waren grundsätzlich niedriger als die Konzentrationen, die in anderen Küstensedimenten des Mittelmeeres und entlang der Küste von Alexandria gemessen wurden waren die gefundenen Gehalte an PAKs in den Muscheln der Abu Qir Bucht waren im Vergleich zu den Muschelarten weltweit sehr hoch.

Die ökologische Risikobewertung (**S**creening **L**evel **E**cological **R**isk **A**ssessment) zeigt, dass Hg, Zn, Cd, DDDs, DDTs, Dieldrin, Chlordan, Lindan, Heptachlor (PEC HQ $>$ 1), Pb, p-p-DDE und p,p-DDT (TEC HQ > 1 > PEC HQ) als potentielle Verunreinigungen auftreten können und adverse ökologische Effekte für Benthos verursachen, wenn sie in die Bucht eingebracht werden. Auch Endosulfan, Chlorpyrifos, Heptachlorepoxid, welche nur auf der Basis von Orientierungswerten evaluiert wurden, zeigten sich als Schadstoffe, denen im Rahmen eines detaillierten Risk Assement besondere Aufmerksamkeit gewidmet werden sollte. Die Konzentrationen von Aldrin und HCBs waren geringer als der PEC und für beide Schadstoffe war kein TEC verfügbar. Daher wäre es zweckmäßig, dieses in weitergehenden Studien zu untersuchen. Auf der anderen Seite müssen für As, Cr, PCBs, PCBz, Methoxychlor, α-HCH und PAK keine weiteren ausführlichen Studien durchgeführt werden, da keine nachteiligen ökologischen Effekte durch die Exposition dieser Schadstoffe erwartet werden.

Die in den Muscheln gefundenen Konzentrationen an As, Cd, Cu, Hg und Zn sind höher als die Toxizitätsrichtwerte, die auf den Schutz von 95% der benthischen Arten zielen. Daher können Effekte auf benthische Arten nicht ausgeschlossen werden. Andererseits liegen die Konzentrationen aller untersuchten Schadstoffe unterhalb der toxischen Werte für *Mytilus edulis* und *Mytilus galloprovincialis*.

Das **H**uman **H**ealth **R**isk **A**ssessment hat gezeigt, dass durch die Aufnahme der beiden Muschelarten keine kanzerogenen und nicht kanzerogenen Wirkungen für den Menschen zu befürchten sind. Eine Ausnahme bildet As, für das die Berechnungen des Krebsrisikos in *Mactra corallina* Werte zwischen 10^{-6} und 10^{-4} ergaben. Diese Werte liegen im Bereich der durch die EPA festgelegten Schwellenwerte.

Verglichen mit anderen Lebensmitteln, die typischerweise in Ägypten verzehrt werden, gehen gesundheitsschädigende Effekte eher von anderen Lebensmitteln wie Fisch, Brot, Fleisch und Gemüse aus.

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Appendix I

Table A1: Location of sampling sites, water depth, and pH in Abu Qir Bay.

Sample No.	Sample ID	Location		Water depth (m)	Sediment pH
		Longitude	Latitude		
1	S1	31° 17.044'	30° 5.403'	3.0	6.92
2	S2	31° 16.550'	30° 6.018'	3.3	6.90
3	S3	31° 16.301'	30° 8.084'	4.0	6.85
4	SB4	31° 16.314'	30° 10.630'	4.0	6.99
5	S5	31° 19.803'	30° 6.760'	7.0	7.25
6	S6	31° 19.262'	30° 7.483'	6.0	7.38
7	S7	31° 19.307'	30° 6.001'	5.3	7.39
8	SB8	31° 17.216'	30° 10.600'	6.0	7.21
9	SB9	31° 17.908'	30° 10.626'	7.5	7.09
10	S10	31° 18.639'	30° 10.613'	8.5	7.08
11	S11	31° 18.076'	30° 9.365'	9.0	7.21
12	SB12	31° 17.368'	30° 9.334'	5.5	7.32
13	SB13	31° 16.210'	30° 9.337'	4.0	7.58
14	S14	31° 18.699'	30° 9.218'	5.8	7.42
15	S15	31° 17.535'	30° 8.039'	7.0	7.48
16	S16	31° 17.978'	30° 8.081'	5.9	7.39
17	S17	31° 18.809'	30° 7.961'	6.4	7.90
18	SB18	31° 17.918'	30° 7.312'	7.0	7.93
19	SB19	31° 16.552'	30° 7.134'	4.5	8.00
20	S20	31° 17.121'	30° 6.042'	3.0	8.06
21	S21	31° 17.644'	30° 5.408'	2.5	7.70
22	S22	31° 18.271'	30° 5.406'	3.5	7.78
23	S23	31° 18.004'	30° 6.040'	5.5	7.99
24	S24	31° 18.942'	30° 6.060'	6.0	8.10
25	SB25	31° 17.533'	30° 4.760'	2.5	7.19
26	SB26	31° 18.600'	30° 4.334'	2.0	7.28
27	SB27	31° 19.112'	30° 4.927'	2.5	7.11
28	SB28	31° 18.600'	30° 4.716'	2.8	7.20
29	SB29	31° 18.254'	30° 4.350'	3.0	7.48
30	SB30	31° 18.060'	30° 4.287'	2.0	7.75

S = surfacial sediment sample; SB = surfacial and mussel sample.

Table A2: Recovery rates in % of PCBs, PCBz and HCBz fortified to sediments and measured by GC/ECD.

	2 µg/kg dw (n = 4)				25 µg/kg dw (n = 4)			
	Min	**Max**	**Mean**	**RSD (%)**	**Min**	**Max**	**Mean**	**RSD (%)**
PCBz	86.5	97.6	91.0	1.13	81.7	90.0	84.4	4.48
HCBz	91.3	102	96.1	5.28	86.8	95.7	89.5	4.61
PCB 28	97.3	106	103	3.63	91.3	100	94.6	4.15
PCB 52	85.3	98.4	91.8	5.92	105	106	106	0.360
PCB 101	90.6	104	97.5	7.08	85.8	107	96.8	9.10
PCB 153	99.0	108	105	4.24	79.8	107	98.1	12.8
PCB 138	90.7	94.4	92.8	1.85	93.7	107	98.6	6.22
PCB 180	102	106	103	2.14	93.9	98.9	96.4	2.40

Table A3: Recovery rates in % of PAHs fortified to sediments and measured by GC/MS.

	10 µg/kg dw (n = 4)				50 µg/kg dw (n = 4)			
	Min	**Max**	**Mean**	**RSD (%)**	**Min**	**Max**	**Mean**	**RSD (%)**
Nap	71.7	72.7	72.4	0.632	72.6	109	91.3	16.8
Acy	64.2	93.8	78.0	15.6	75.8	113	95.0	15.9
Ace	70.7	81.6	74.3	6.65	75.4	114	96.7	16.8
Flr	81.2	110	101	13.4	83.6	114	98.3	15.0
Phn	88.9	93.5	92.8	3.56	76.6	117	98.0	17.2
Ant	91.4	114	99.2	10.5	73.2	117	93.4	19.5
Fla	78.3	86.4	83.1	4.50	86.6	106	98.0	8.39
Pyr	74.6	88.5	80.7	7.80	77.1	114	90.0	18.1
BaA	91.8	102	98.0	5.01	88.0	109	96.9	9.22
Chy	79.8	91.2	94.9	5.75	68.6	98.4	86.1	15.7
BbF	74.0	82.6	76.8	5.13	76.2	109	95.3	17.1
BkF	73.7	85.5	77.8	6.83	89.9	106	97.4	8.46
BaP	94.6	106	98.4	5.48	89.1	110	95.3	10.0
InP	81.8	91.5	85.1	5.26	88.2	107	96.9	7.90
DibA	82.1	89.5	86.1	4.00	79.4	113	90.5	16.8
BghiP	80.4	89.8	85.9	5.30	89.1	107	96.3	8.15

Table A4: Recovery rates in % of pesticides fortified to sediments and measured by GC/ECD.

	2 µg/kg dw (n = 4)				25 µg/kg dw (n = 4)			
	Min	**Max**	**Mean**	**RSD (%)**	**Min**	**Max**	**Mean**	**RSD (%)**
α-HCH	79.0	87.5	80.0	8.54	86.9	95.5	92.1	3.96
β-HCH	81.5	105	93.6	10.4	100	110	109	0.960
γ-HCH	76.2	89.4	82.2	7.10	93.3	103	98.9	4.06
δ-HCH	77.0	93.2	85.3	8.28	101	110	106	3.32
Heptachlor	111	118	114	2.67	80.5	101	92.0	10.3
Chlorpyrifos	70.0	91.1	80.1	13.4	83.9	103	89.7	10.1
Aldrin	85.9	96.3	90.0	5.24	95.9	107	99.1	5.32
Cis-epoxide	78.2	100	89.9	10.3	101	113	105	7.01
Trans-epoxide	86.6	111	99.5	10.3	97.4	104	100	2.64
Trans-chlord.	92.6	109	99.3	7.71	95.9	108	103	5.27
Cis-chlordane	78.6	103	92.3	11.0	88.1	101	93.0	6.31
α-endosulfane	78.8	101	91.2	10.4	100	110	104	3.90
β-endosulfane	79.9	95.8	87.7	1.56	99.8	106	102	6.07
o,p'-DDE	78.8	102	91.1	10.6	86.7	96.7	91.2	4.58
p,p'-DDE	81.3	86.4	83.7	2.55	86.4	91.7	89.6	2.84
Dieldrin	71.3	80.2	75.4	4.90	94.9	104	99.0	3.81
o,p'-DDD	74.9	98.3	86.0	11.7	90.0	104	91.2	7.63
p,p'-DDD	82.3	101	90.6	10.1	94.4	104	98.8	4.07
o.p'-DDT	89.6	103	96.9	5.98	82.5	96.7	90.5	7.43
p,p'-DDT	75.2	97.9	54.7	11.2	91.3	99.4	95.5	3.49
Methoxychlor	70.7	97.5	81.9	14.4	84.6	103	97.4	8.85
Mirex	88.6	98.6	94.3	5.41	91.8	100	95.6	3.59

TableA5: Recovery rates in % of PCBs, PCBz and HCBz fortified to mussel tissues and measured by GC/ECD.

	5.5 µg/kg ww (n = 4)				55 µg/kg ww (n = 4)			
	Min	**Max**	**Mean**	**RSD (%)**	**Min**	**Max**	**Mean**	**RSD (%)**
PCBz	74.8	90.6	83.4	9.72	85.2	107	95.9	9.36
HCBz	74.2	85.7	81.4	6.75	81.3	91.1	86.0	4.78
PCB 28	85.8	103	96.2	7.64	83.3	93.3	88.9	4.38
PCB 52	94.3	100	96.5	2.70	80.9	96.1	89.2	7.05
PCB 70	84.3	111	97.0	12.4	85.8	92.8	88.2	3.53
PCB 101	83.7	109	96.0	12.2	84.8	93.1	88.0	4.05
PCB 118	82.3	89.8	85.5	3.65	83.3	101	92.3	8.00
PCB 153	89.6	107	97.8	7.36	80.3	97.0	89.6	8.49
PCB 138	93.1	97.5	94.7	2.13	78.9	98.9	89.2	9.33
PCB 126	73.2	89.9	80.0	10.0	79.2	89.5	84.3	4.98
PCB 156	85.0	93.7	89.0	4.08	73.2	88.7	80.0	8.04
PCB 180	84.1	96.3	89.3	7.01	85.2	101	92.6	8.38
PCB 169	73.1	80.2	76.1	4.01	70.5	91.5	81.9	10.6

Table A6: Recovery rates in % of PAHs fortified to mussel tissues and measured by GC/MS.

	25 µg/kg ww (n = 4)				100 µg/kg ww (n = 4)			
	Min	**Max**	**Mean**	**RSD (%)**	**Min**	**Max**	**Mean**	**RSD (%)**
Nap	81.6	97.9	86.6	8.72	74.7	90.1	81.5	9.00
Acy	78.7	98.7	85.1	10.9	75.1	85.6	81.0	6.03
Ace	75.3	93.7	81.1	10.5	76.0	86.9	81.5	6.06
Flr	72.1	92.2	78.0	12.3	71.6	80.7	76.6	6.32
Phn	92.8	113	98.7	9.42	84.4	97.0	90.6	6.08
Ant	86.1	104	91.5	9.00	82.7	93.4	88.3	5.42
Fla	115	118	116	0.982	91.4	103	96.1	5.54
Pyr	104	117	109	5.08	91.9	106	97.9	6.68
BaA	97.1	112	104	5.83	87.6	102	94.5	6.11
Chy	105	119	113	5.31	99.0	117	108	6.84
BbF	96.2	112	103	6.64	90.0	103	95.4	5.51
BkF	92.4	107	97.6	6.70	85.6	99.1	92.4	6.00
BaP	106	109	107	1.62	89.3	103	95.9	5.81
InP	104	114	109	3.64	86.7	100	93.1	5.97
DibA	87.1	101	93.5	6.36	104	113	110	3.58
BghiP	87.5	103	94.4	7.05	105	112	108	2.98

Table A7: Recovery rates in % of pesticides fortified to mussel tissues and measured by GC/ECD.

	5.5 µg/kg ww (n = 4)				55 µg/kg ww (n = 4)			
	Min	**Max**	**Mean**	**RSD (%)**	**Min**	**Max**	**Mean**	**RSD (%)**
α-HCH	92.6	97.3	94.7	2.29	88.5	90.7	90.0	1.09
β-HCH	99.4	106	102	3.00	97.3	100	99.5	0.87
γ-HCH	93.5	100	96.5	3.26	97.6	100	99.2	1.16
δ-HCH	101	108	104	3.54	95.4	103	98.7	3.09
Heptachlor	103	108	105	2.52	89.4	112	103	9.10
Chlorpyrifos	78.3	97.9	86.9	9.34	105	106	105	0.467
Aldrin	74.2	97.3	83.7	12.7	90.2	106	96.9	7.35
Cis-epoxide	80.2	83.4	81.4	1.75	Na	Na	Na	Na
Trans-epoxide	83.1	103	97.5	9.90	Na	Na	Na	Na
Trans-chlord.	88.7	93.5	91.7	2.41	84.9	87.6	86.5	1.47
Cis-chlordane	96.8	102	99.0	2.53	94.0	97.4	95.8	1.59
α-endosulfan	99.1	107	103	3.62	99.8	101	100	0.51
β-endosulfan	96.7	106	101	2.56	103	105	104	5.53
o,p'-DDE	75.8	78.8	77.1	2.00	76.6	78.8	77.6	1.28
p,p'-DDE	84.7	90.1	87.0	2.90	102	109	105	2.69
Dieldrin	86.2	90.0	88.1	2.25	95.3	98.6	96.8	1.50
o,p'-DDD	89.9	99.6	94.2	4.30	103	106	105	1.09
p,p'-DDD	82.7	88.7	85.3	3.51	98.1	101	99.1	1.23
o.p'-DDT	88.7	94.7	91.7	3.31	89.6	96.9	93.0	3.44
p,p'-DDT	75.8	103	96.7	6.22	84.2	95.4	88.9	5.68
Methoxychlor	90.1	109	97.3	8.98	99.2	109	104	4.02
Mirex	86.1	106	93.9	9.22	90.2	109	99.1	10.3

Na: not analyzed

Table A8: MDL of trace metals measured by ICP-OES and ICP-MS.

	ICP-OES	ICP-MS
Element	**Detection limit (mg/L)**	
Al	0.100	NA
As*	0.0006	0.002
Cd	0.005	0.001
Co	0.01	Na
Cr	0.02	0.02
Cu	0.01	0.001
Fe	0.200	Na
Hg**	0.01	Na
Mn	0.005	0.003
Ni	0.01	Na
Pb	0.03	0.002
Se*	0.0005	0.001
Sn	0.05	Na
V	0.01	Na
Zn	0.02	0.1

*: As and Se were measured with the hydride generation technique (ICP-OES)
**: Hg was measured with the cold vapour technique (ICP-OES)
Na: not analyzed

Table A9: Method detection limit (MDL) for PCBz, HCBz and PCBs in sediments and mussels measured by GC/ECD.

	Sediments			Mussels		
	MDL (µg/kg dw)	**RSD (%)**	**Average recovery (%) (n = 7)**	**MDL (µg/kg dw)**	**RSD (%)**	**Average recovery (%) (n = 7)**
PCBz	0.083	6.44	81.7	0.208	4.69	100
HCBz	0.102	7.78	83.7	0.258	5.93	98.8
PCB 28	0.146	7.66	86.8	0.168	4.19	91.1
PCB 52	0.183	6.49	100	0.367	8.94	93.0
PCB 70	0.396	13.6	102	0.292	7.92	83.4
PCB 101	0.082	9.92	88.2	0.543	14.6	83.1
PCB 118	0.279	15.2	83.5	0.214	6.04	80.1
PCB 153	0.168	9.66	77.5	0.418	10.8	89.7
PCB 138	0.111	8.26	83.5	0.307	8.40	85.3
PCB 126	0.109	13.2	88.0	0.444	11.8	85.1
PCB 156	0.255	15.4	88.2	0.257	7.53	77.3
PCB 180	0.101	6.71	95.2	0.208	4.69	100
PCB 169	0.096	10.5	97.3	0.258	5.93	98.8

Table A10: Method detection limit (MDL) for PAHs in sediments and mussels measured by GC/MS.

	Sediments			Mussels		
	MDL (µg/kg dw)	RSD (%)	Average recovery (%) (n = 7)	MDL (µg/kg dw)	RSD (%)	Average recovery (%) (n = 7)
Nap	3.18	14.0	96.1	2.56	10.9	81.4
Acy	2.73	13.4	86.3	1.07	4.70	79.2
Ace	3.75	19.4	82.0	2.51	4.56	88.8
Flr	2.01	8.52	100	3.62	7.33	78.6
Phn	2.93	11.8	98.4	2.02	3.04	106
Ant	2.60	11.3	98.0	2.97	5.02	94.2
Fla	1.26	6.69	79.7	2.42	3.34	116
Pyr	1.62	8.30	82.8	3.23	4.38	117
BaA	2.63	11.7	95.6	3.04	4.60	105
Chy	2.59	12.2	90.2	5.20	8.73	94.9
BbF	1.61	8.11	75.8	1.75	2.58	108
BkF	1.79	8.89	85.4	3.94	6.29	99.8
BaP	1.89	9.56	84.1	2.12	7.96	102
InP	2.83	12.4	97.2	10.2	16.4	98.9
DibA	3.34	15.0	94.3	8.49	16.9	79.8
BghiP	2.72	12.0	96.1	5.78	9.41	97.8

Table A11: Method detection limit (MDL) for pesticides in sediments and mussels measured by GC/ECD.

	Sediments			Mussels		
	MDL (µg/kg dw)	RSD (%)	Average recovery (%) (n = 7)	MDL (µg/kg dw)	RSD (%)	Average recovery (%) (n = 7)
α-HCH	0.152	5.94	102	0.421	10.5	90.8
β-HCH	0.227	11.9	86.6	0.248	5.77	97.3
γ-HCH	0.168	8.11	94.0	0.455	11.4	90.7
δ-HCH	0.150	6.77	101	0.389	8.82	100
Heptachlor	0.220	11.7	85.6	0.170	3.78	101
Chlorpyrifos	0.379	7.51	80.3	0.283	6.39	101
Aldrin	0.177	8.65	93.3	0.312	8.27	85.5
Cis-epoxide	0.250	12.4	91.4	0.319	6.37	114
Trans-epoxide	0.226	14.4	83.0	0.271	5.42	114
Trans-chlord.	0.369	16.4	102	0.376	8.96	95.2
Cis-chlordane	0.271	14.1	87.3	0.412	10.4	90.0
α-endosulfan	0.191	9.67	89.7	0.427	10.0	96.9
β-endosulfan	0.134	8.93	95.3	0.280	6.42	98.9
o,p'-DDE	0.256	18.8	86.6	0.459	12.5	83.1
p,p'-DDE	0.178	8.39	96.3	0.253	5.86	97.8
Dieldrin	0.262	14.8	80.7	0.323	8.31	88.2
o,p'-DDD	0.161	18.1	94.4	0.299	7.14	94.9
p,p'-DDD	0.071	8.86	84.9	0.383	9.35	92.9
o.p'-DDT	0.136	16.6	87.0	0.641	15.0	96.9
p,p'-DDT	0.072	7.12	107	0.795	19.0	94.9
Methoxychlor	0.071	6.90	109	0.737	16.5	101
Mirex	0.120	12.4	103			

Table A12: Concentrations of metals obtained from the analysis with ICP-OES of the certified sediment reference material (BCR: CRM-320-river sediment) and their recoveries in %.

Element	Certified value (mg/kg)	Determined value (mg/kg) (n = 3)	Recovery (%)
Al	(82000)	77540 ± 140	94.6
As	76.4 ± 3.4	75.324 ± 0.329	98.6
Cd	0.533 ± 0.026	0.524 ± 0.027	98.3
Co	(19)	18 ± 0.85	94.7
Cr	138 ± 7	132.2 ± 1.5	95.9
Cu	44.1 ± 1	43.5 ± 0.6	98.6
Fe	(45000)	43428 ± 180	96.5
Hg	1.03 ± 0.16	1.069 ± 0.096	104
Mn	(800)	777 ± 20	97.1
Ni	75.2 ± 1.4	76.4 ± 0.5	102
Pb	42.3 ± 1.6	42.9 ± 1	101
Se	0.214 ± 0.034	0.218 ± 0.011	102
Sn	(6)	6.2 ± 0.55	103
V	(5000)	4750 ± 60	95.0
Zn	(105)	102 ± 5	97.1

( ): Values between brackets are uncertified.

Table A13: Concentrations of metals obtained from the analysis with ICP-MS of the certified mussel reference material (BCR: ERM-CE278 mussel tissues) and their recoveries in %.

Element	Certified values (mg/kg)	Determined values (mg/kg) (n = 3)	Recovery (%)
As	6.07 ± 0.13	6.25 ± 0.340	103
Cd	0.348 ± 0.007	0.33 ± 0.018	96.0
Cr	0.78 ± 0.06	0.88 ± 0.062	113
Cu	9.45 ± 0.13	9.13 ± 0.41	97.0
Hg	0.196 ± 0.009	0.19 ± 0.005	99.0
Mn	7.69 ± 0.23	7.62 ± 0.69	99.0
Pb	2.0 ± 0.04	1.9 ± 0.14	95.0
Se	1.84 ± 0.1	1.83 ± 0.25	99.6
Zn	83.1 ± 1.7	79.07 ± 4.7	95.0

Table A14: Average RSD for the investigated trace elements in sediment and mussel samples Abu Qir Bay.

	RSD (%) (n = 2)	
	Sediments	**Mussels**
Al	10.0	
As	5.00	2.61
Cd	6.00	10.1
Co	7.00	
Cr	8.00	11.8
Cu	8.00	6.13
Fe	9.00	
Hg	11.0	9.50
Mn	5.00	1.90
Ni	7.00	
Pb	8.00	5.60
Se	8.00	11.8
Sn	11.0	
V	5.00	
Zn	7.00	3.66

Table A15: Average RSD for the investigated PAHs in sediment and mussel samples Abu Qir Bay.

	RSD (%) (n = 2)	
	Sediments	**Mussels**
Nap	11.4	5.00
Acy	10.5	2.90
Ace	10.1	4.70
Flr	9.60	4.90
Phn	5.63	10.4
Ant	6.87	4.37
Fla	7.22	7.36
Pyr	4.33	3.04
BaA	9.36	10.2
Chy	5.58	6.80
BbF	8.84	1.26
BkF	5.15	0.710
BaP	4.38	0.800
InP	9.55	5.63
DibA	8.77	0.800
BghiP	7.81	0.940

Table A16: Average RSD for the investigated PCBs, PCBz and HCBz in sediment and mussel samples Abu Qir Bay.

	RSD (%) (n = 2)	
	Sediments	**Mussels**
PCBz	7.39	6.33
HCBz	5.88	4.63
PCB 28	4.68	1.08
PCB 52	9.55	4.60
PCB 70	7.74	3.00
PCB 101	3.35	0.800
PCB 118	4.97	1.65
PCB 153	5.42	1.11
PCB 138	2.26	1.70
PCB 126	9.97	0.800
PCB 156	10.5	9.90
PCB 180	4.78	1.53
PCB 169	8.71	ND

ND: not detected

Table A17: Average RSD for the investigated pesticides in sediment and mussel samples Abu Qir Bay.

	RSD (%) (n = 2)	
	Sediments	**Mussels**
α-HCH	11.6	8.47
β-HCH	9.39	5.36
γ-HCH	10.5	7.09
δ-HCH	8.41	6.17
Heptachlor	6.64	9.55
Chlorpyrifos	7.54	3.17
Aldrin	11.3	5.11
Cis-epoxide	8.47	6.60
Trans-epoxide	9.81	7.38
Trans-chlord.	9.74	8.11
Cis-chlordane	11.1	7.95
α-endosulfan	7.54	4.18
β-endosulfan	8.15	5.55
o,p'-DDE	9.63	8.01
p,p'-DDE	10.1	8.88
Dieldrin	9.77	7.61
o,p'-DDD	8.41	5.58
p,p'-DDD	6.62	6.35
o.p'-DDT	11.8	10.8
p,p'-DDT	11.5	11.6
Methoxychlor	9.08	10.5
Mirex	6.91	5.17

Table A18: Water content (WC), $CaCO_3$, total organic carbon (TOC) content and sediment particle size distribution by weight % in surfacial sediments of Abu Qir Bay.

Station No.	WC (%)	$CaCO_3$ (%)	TOC (%)	Sand (%)	Silt (%)	Clay (%)	Silt + clay (%)
1	49.6	33.8	5.79	66.0	20.0	14.1	34.1
2	57.4	34.1	6.23	27.4	40.2	32.4	72.6
3	48.6	17.6	0.468	62.0	20.0	18.0	38.0
4	43.2	18.2	0.588	11.3	73.4	15.3	88.7
5	15.9	45.7	0.0930	97.7	1.74	0.600	2.34
6	17.2	26.5	0.0220	98.3	0.741	0.960	1.70
7	18.7	39.4	0.0820	98.3	0.748	1.00	1.74
8	44.4	34.0	1.12	64.0	22.0	14.0	36.0
9	32.0	30.2	0.0010	91.0	6.00	3.75	9.75
10	28.9	27.8	0.0210	96.0	1.00	3.25	4.25
11	20.8	28.6	0.140	96.1	1.55	2.32	3.86
12	22.4	31.1	0.0230	92.0	3.67	4.33	8.00
13	41.0	20.5	0.0520	48.0	44.0	8.00	52.0
14	22.5	29.1	2.42	91.0	7.00	2.00	9.00
15	34.6	24.9	0.0300	38.5	46.5	15.0	61.5
16	25.0	22.4	0.0500	85.4	10.6	3.99	14.6
17	19.6	16.1	0.105	84.0	11.7	4.33	16.0
18	21.6	33.7	0.0340	71.2	24.5	4.33	28.8
19	25.4	42.5	0.293	82.9	8.70	8.36	17.1
20	42.5	36.6	1.47	7.80	79.9	12.3	92.2
21	41.5	31.0	12.13	43.7	37.3	19.0	56.3
22	19.2	35.4	0.162	92.6	2.38	5.06	7.45
23	23.8	47.9	0.368	90.0	4.66	5.32	9.98
24	21.6	46.3	0.0290	91.8	1.90	6.33	8.23
25	20.7	23.7	0.0140	95.0	1.75	3.24	4.99
26	18.9	18.2	0.0310	96.7	1.00	2.26	3.26
27	16.2	37.3	0.0240	97.1	0.748	2.24	2.99
28	18.0	25.2	0.417	96.6	1.55	1.81	3.35
29	20.6	26.3	0.0050	95.0	2.00	3.00	5.00
30	21.0	31.7	0.0110	94.8	2.64	2.64	5.27
Min.	**15.9**	**16.1**	**0.001**	**7.78**	**0.741**	**0.600**	**1.70**
Max.	**57.4**	**47.9**	**12.1**	**98.3**	**79.9**	**32.4**	**92.2**
Mean	**28.4**	**30.5**	**1.07**	**76.7**	**16.0**	**7.31**	**23.3**
St. dev.	**11.9**	**8.61**	**2.59**	**27.0**	**21.6**	**7.23**	**27.0**

Table A19: Concentrations of trace metals (mg/kg dw), Al and Fe (% dw) in surfacial sediments of Abu Qir Bay.

Station No.	Al (%)	Fe (%)	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Sn	V	Zn
1	1.01	1.65	7.18	1.86	9.60	42.6	52.7	1.70	372	18.1	26.6	1.25	2.19	58.5	213
2	4.64	3.71	11.0	3.54	22.8	186	127	2.70	582	40.5	127	2.18	6.50	118	717
3	2.16	3.02	4.31	1.47	19.8	129	16.4	0.648	459	33.6	129	2.02	7.30	129	103
4	2.88	2.50	8.17	3.17	21.2	86.5	17.3	1.54	394	31.7	96.2	2.01	12..6	106	79.8
5	0.0171	0.144	1.13	0.0822	<DL	5.48	<DL	0.548	151	2.05	3.29	0.340	4.45	12.3	7.53
6	0.0353	0.112	0.650	0.0862	<DL	4.66	<DL	0.431	58.6	3.88	4.14	0.370	3.79	12.1	6.47
7	0.0225	0.387	0.770	<DL	<DL	6.31	<DL	0.450	133	2.25	8.56	0.610	4.05	9.90	5.77
8	2.21	2.21	4.34	1.62	11.1	29.5	25.1	1.50	387	14.0	38.4	1.59	3.54	31.0	69.4
9	1.30	0.593	1.85	1.11	3.43	27.8	3.24	1.48	333	3.43	17.6	2.83	7.32	22.2	24.1
10	0.223	0.669	0.550	0.558	4.22	55.8	3.03	0.956	382	7.65	35.9	1.96	12.1	39.0	23.1
11	0.326	0.703	1.46	1.09	3.68	62.8	3.43	0.669	351	7.03	34.3	2.56	11.1	41.0	21.8
12	0.266	0.635	0.970	0.515	3.00	23.3	3.78	1.37	266	7.04	27.5	1.91	5.60	24.9	20.6
13	1.42	0.376	1.51	1.42	0.993	22.1	2.41	1.42	320	2.13	13.5	1.45	<DL	13.5	9.90
14	0.981	1.96	1.70	0.453	12.8	45.3	38.5	1.51	374	23.4	83.0	2.17	4.91	83.0	106
15	2.86	1.30	3.57	1.17	5.39	45.5	5.65	0.519	383	17.5	64.3	2.46	2.01	55.8	78.0
16	0.339	0.638	0.660	0.797	4.19	49.8	5.18	0.532	279	9.30	27.2	1.32	2.19	42.5	24.6
17	0.224	0.261	0.230	0.667	0.727	18.2	2.06	0.970	152	3.45	6.06	1.42	3.70	12.7	15.8
18	1.10	0.463	3.28	0.706	3.84	47.1	3.53	0.627	310	18.8	16.5	1.84	1.33	52.8	14.1
19	1.21	0.358	1.09	0.969	3.83	60.5	6.78	0.969	358	21.3	53.3	0.930	2.91	78.0	28.1
20	3.03	1.061	4.55	3.18	3.11	37.9	37.9	0.909	397	5.83	53.8	4.00	2.26	28.8	189

<DL: below the limit of detection

Table A19: Continued.

Station No.	Al (%)	Fe (%)	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Sn	V	Zn
21	3.79	0.769	4.05	1.81	2.47	22.0	60.4	1.10	326	6.59	48.9	1.19	1.32	20.9	242
22	1.08	0.736	2.11	0.823	2.81	51.9	8.23	0.519	281	6.06	33.8	0.675	2.77	33.8	32.0
23	1.27	0.660	3.01	1.46	1.84	37.7	10.8	0.566	250	5.19	25.0	0.934	2.12	29.7	44.3
24	1.05	0.306	2.99	0.957	<DL	14.4	3.35	0.766	134	<DL	5.74	1.95	3.45	8.23	12.4
25	0.590	0.157	1.43	0.663	<DL	9.04	2.05	0.241	114	<DL	2.71	1.19	4.22	5.84	6.63
26	1.36	0.391	1.36	0.727	<DL	22.7	1.27	0.273	127	<DL	3.64	2.02	<DL	12.7	8.00
27	0.122	0.251	1.78	0.339	<DL	16.9	0.95	0.271	149	<DL	10.2	1.42	2.72	9.5	8.81
28	0.267	0.224	1.10	0.263	<DL	13.2	3.33	0.263	74.2	<DL	8.60	1.95	2.41	6.23	9.16
29	0.271	0.362	1.12	0.271	<DL	22.6	4.52	0.271	85.2	<DL	13.6	1.85	4.80	10.9	11.8
30	0.304	0.474	1.94	0.444	<DL	18.5	4.96	0.296	193	<DL	19.3	1.96	3.93	14.1	11.1
Min.	**0.0171**	**0.112**	**0.227**	**0.0822**	**0.727**	**4.66**	**0.95**	**0.241**	**58.6**	**2.05**	**2.71**	**0.342**	**1.32**	**5.84**	**5.77**
Max.	**4.64**	**3.71**	**11.0**	**3.54**	**22.8**	**186**	**127**	**2.70**	**582**	**40.5**	**129**	**4.00**	**12.1**	**129**	**717**
Mean	**1.21**	**0.903**	**2.66**	**1.07**	**4.69**	**40.5**	**15.1**	**0.867**	**273**	**9.69**	**34.6**	**1.68**	**4.04**	**37.4**	**71.4**
St. dev.	**1.21**	**0.912**	**2.46**	**0.907**	**6.53**	**38.1**	**26.4**	**0.574**	**131**	**11.1**	**34.7**	**0.768**	**2.78**	**34.2**	**137**

Table A20: Concentrations (mg/kg dw) of selected trace metals obtained after sequential extraction of the surfacial sediments of Abu Qir Bay.

	Exchangeable (F1)	Carbonates (F2)	Reducible (F3)	Oxidizable (F4)	Residual (F5)
Station No.			**Co**		
1	0.929	0.356	2.96	<DL	5.35
2	1.40	0.206	8.05	<DL	13.1
3	0.973	0.000	6.68	<DL	12.1
4	1.08	0.503	8.52	<DL	11.1
8	<DL	0.337	4.71	<DL	6.05
14	1.10	0.609	5.22	<DL	5.87
19	0.284	0.454	<DL	<DL	3.09
20	0.348	0.209	<DL	<DL	2.55
21	0.612	0.242	0.712	<DL	0.904
Min	**<DL**	**<DL**	**<DL**	**-**	**0.904**
Max	**1.40**	**0.609**	**8.52**	**-**	**13.1**
Mean	**0.748**	**0.324**	**4.10**	**-**	**6.69**
S.d	**0.461**	**0.184**	**3.35**	**-**	**4.43**
Station No.			**Cr**		
1	3.22	1.09	15.6	4.15	18.5
2	7.85	0.506	74.7	4.49	98.4
3	4.08	0.706	34.2	4.96	85.1
4	4.07	0.639	32.7	2.71	46.4
8	<DL	0.539	15.0	2.53	11.5
14	1.08	0.661	13.8	12.9	16.9
19	1.02	0.530	28.2	0.189	30.6
20	1.98	0.348	19.0	1.74	14.9
21	2.11	1.17	8.40	4.56	5.77
Min	**<DL**	**0.348**	**8.40**	**0.189**	**5.77**
Max	**7.85**	**1.17**	**74.7**	**12.9**	**98.4**
Mean	**2.82**	**0.687**	**26.8**	**4.25**	**36.4**
S.d	**2.35**	**0.271**	**20.1**	**3.59**	**33.7**
Station No.			**Cu**		
1	8.30	0.573	11.1	16.8	16.0
2	13.6	<DL	15.9	61.8	35.7
3	3.13	<DL	3.63	4.96	4.68
4	3.39	<DL	2.71	6.97	4.23
8	<DL	<DL	2.19	5.05	17.9
14	5.43	<DL	11.3	17.4	4.35
19	1.63	<DL	<DL	3.22	1.94
20	5.93	<DL	7.30	14.1	10.6
21	12.5	1.71	15.7	22.8	7.80
Min	**<DL**	**<DL**	**<DL**	**3.22**	**1.94**
Max	**13.6**	**1.71**	**15.9**	**61.8**	**35.7**
Mean	**5.98**	**0.253**	**7.75**	**17.0**	**11.5**
S.d	**4.68**	**0.578**	**5.98**	**18.1**	**10.6**

<DL = below the detection limit

Table A20: Continued.

	Exchangeable (F1)	Carbonates (F2)	Reducible (F3)	Oxidizable (F4)	Residual (F5)
Station No.			**Fe**		
1	0.257	23.7	8300	1522	6643
2	9.81	7.12	17416	1236	16272
3	<DL	89.7	10878	420	16420
4	<DL	180	12004	794	10509
8	<DL	60.6	7744	589	12292
14	<DL	14.1	7659	2785	10139
19	<DL	142	1798	757	1314
20	0.383	3.48	3130	939	6493
21	2.73	65.5	3132	1153	3782
Min	**<DL**	**3.48**	**1798**	**420**	**1314**
Max	**9.81**	**180**	**17416**	**2785**	**16420**
Mean	**1.47**	**65.1**	**8007**	**1133**	**9318**
S.d	**3.25**	**62.5**	**4989**	**706**	**5239**
Station No.			**Mn**		
1	9.29	98.8	77.1	13.8	173
2	6.35	41.2	225	11.0	299
3	11.6	84.0	72.5	7.44	283
4	18.0	176	60.0	11.0	129
8	28.6	219	82.5	7.58	49.5
14	40.2	244	24.4	34.8	30.9
19	16.8	148	88.9	8.14	96.6
20	9.51	36.5	45.2	7.83	298
21	9.18	38.4	51.2	11.2	216
Min	**6.35**	**36.5**	**24.4**	**7.44**	**30.9**
Max	**40.2**	**244**	**225**	**34.8**	**299**
Mean	**16.6**	**121**	**80.7**	**12.6**	**175**
S.d	**11.1**	**79.5**	**57.7**	**8.63**	**105**
Station No.			**Ni**		
1	1.56	1.48	5.53	<DL	9.52
2	0.899	0.543	17.0	<DL	22.0
3	0.439	<DL	10.3	<DL	22.9
4	0.736	<DL	13.0	<DL	18.0
8	0.118	<DL	7.74	<DL	6.14
14	0.592	0.627	12.0	8.70	1.47
19	0.454	<DL	9.08	<DL	11.8
20	0.591	<DL	<DL	<DL	5.24
21	1.01	1.17	<DL	<DL	4.41
Min	**0.118**	**<DL**	**<DL**	**<DL**	**1.50**
Max	**1.56**	**1.48**	**17.0**	**8.70**	**22.9**
Mean	**0.711**	**0.424**	**8.30**	**0.967**	**11.3**
S.d	**0.414**	**0.573**	**5.73**	**2.90**	**7.94**

<DL = below the detection limit

Table A20: Continued.

	Exchangeable (F1)	Carbonates (F2)	Reducible (F3)	Oxidizable (F4)	Residual (F5)
Station No.			**Pb**		
1	8.10	2.96	11.1	<DL	4.47
2	21.7	2.25	86.1	<DL	16.9
3	16.6	0.840	91.6	<DL	19.9
4	17.8	0.949	56.1	<DL	21.3
8	<DL	1.18	6.40	<DL	30.8
14	8.89	1.67	43.5	5.22	23.7
19	9.21	0.965	20.8	<DL	22.3
20	8.63	1.60	13.4	<DL	30.2
21	10.7	3.56	10.7	<DL	23.9
Min	**<DL**	**0.840**	**6.40**	**<DL**	**4.47**
Max	**21.7**	**3.56**	**91.6**	**5.22**	**30.8**
Mean	**11.3**	**1.77**	**37.8**	**0.580**	**21.5**
S.d	**6.47**	**0.964**	**33.4**	**1.74**	**7.80**
Station No.			**V**		
1	0.534	0.771	27.7	3.36	26.2
2	12.1	1.01	61.8	2.81	40.3
3	<DL	0.210	43.9	2.48	82.4
4	<DL	0.252	48.4	2.90	54.4
8	<DL	<DL	18.5	<DL	12.5
14	0.348	0.209	33.1	12.4	37.0
19	<DL	<DL	37.8	2.46	37.7
20	0.609	0.748	13.4	1.74	12.3
21	0.854	0.811	11.2	3.99	4.00
Min	**<DL**	**<DL**	**11.3**	**<DL**	**4.00**
Max	**12.1**	**1.01**	**61.8**	**12.4**	**82.4**
Mean	**1.61**	**0.446**	**32.9**	**3.57**	**34.1**
S.d	**3.95**	**0.387**	**17.0**	**3.48**	**24.3**
Station No.			**Zn**		
1	60.5	51.4	47.4	<DL	57.7
2	163	52.4	225	1.12	103
3	24.2	11.5	32.4	<DL	13.9
4	25.4	11.2	<DL	<DL	54.4
8	6.94	8.59	30.3	<DL	1.86
14	30.1	20.9	22.6	<DL	30.6
19	6.23	11.7	<DL	<DL	21.9
20	71.7	47.0	31.3	<DL	54.7
21	91.5	85.4	14.0	<DL	123
Min	**6.23**	**8.59**	**<DL**	**<DL**	**1.86**
Max	**163**	**85.4**	**225**	**1.12**	**123**
Mean	**53.3**	**33.3**	**44.8**	**0.125**	**51.2**
S.d	**50.5**	**26.9**	**69.3**	**0.375**	**40.3**

<DL = below the detection limit

Table A21: Enrichment factors calculated for trace metals in surfacial sediments of Abu Qir Bay.

Station No.	Fe	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Sn	V	Zn
1	2.8	4.4	67.0	4.0	3.7	9.3	74.9	3.5	2.1	10.5	164	2.9	3.6	17.8
2	1.4	1.5	27.7	2.1	3.6	4.9	25.9	1.2	1.0	10.9	62.6	1.9	1.6	13.0
3	2.4	1.2	24.7	3.9	5.3	1.3	13.3	2.0	1.8	23.9	125	4.5	3.7	4.0
4	1.5	1.7	40.0	3.1	2.7	1.1	23.7	1.3	1.3	13.4	93.0	2.8	2.3	2.3
8	1.7	1.2	26.7	2.1	1.2	2.0	30.0	1.6	0.7	7.0	96.2	2.1	0.9	2.6
9	0.8	0.9	31.0	1.1	1.9	0.4	51.0	2.4	0.3	5.4	291	7.5	1.1	1.6
10	5.1	1.5	91.0	8.0	22.2	2.4	191	16.1	4.0	64.4	1172	72.3	10.8	8.7
11	3.7	2.8	122	4.8	17.1	1.9	91.0	10.1	2.5	42.1	1047	45.4	7.7	5.6
12	4.1	2.2	70.4	4.7	7.8	2.5	229	9.4	3.1	41.4	955	28.1	5.8	6.5
13	0.5	0.7	36.4	0.3	1.4	0.3	44.0	2.1	0.2	3.8	136	ND	0.6	0.6
14	3.4	1.1	16.8	5.5	4.1	7.0	68.0	3.6	2.8	33.8	296	6.7	5.2	9.1
15	0.8	0.8	14.9	0.8	1.4	0.4	8.1	1.3	0.7	9.0	115	0.9	1.2	2.3
16	3.2	1.2	85.5	5.2	13.1	2.7	70.0	7.7	3.2	32.1	518	8.6	7.7	6.1
17	2.0	0.6	108	1.4	7.2	1.6	193	6.4	1.8	10.8	844	22.0	3.5	5.9
18	0.7	1.8	23.3	1.5	3.8	0.6	25.0	2.7	2.0	6.0	222	1.6	2.9	1.1
19	0.5	0.6	29.1	1.3	4.4	1.0	36.0	2.8	2.1	17.6	103	3.2	4.0	2.0
20	0.6	0.9	38.2	0.4	1.1	2.2	13.0	1.2	0.2	7.1	176	1.0	0.6	5.3
21	0.3	0.7	17.4	0.3	0.5	2.8	12.9	0.8	0.2	5.2	41.8	0.5	0.3	5.4
22	1.2	1.2	27.7	1.1	4.3	1.4	21.4	2.4	0.7	12.5	83.3	3.4	1.9	2.5
23	0.9	1.5	41.8	0.6	2.6	1.5	19.8	1.9	0.5	7.9	98.1	2.2	1.4	2.9
24	0.5	1.8	33.1	ND	1.2	0.6	32.4	1.2	ND	2.2	248	4.4	0.5	1.0
25	0.5	1.5	40.9	ND	1.4	0.6	18.2	1.8	ND	1.8	270	9.5	0.6	0.9
26	0.5	0.6	19.4	ND	1.5	0.2	8.9	0.9	ND	1.1	198	ND	0.6	0.5
27	3.5	9.0	101	ND	12.3	1.4	98.7	11.5	ND	33.4	1556	29.7	4.8	6.1
28	1.4	2.5	35.8	ND	4.4	2.2	43.8	2.6	ND	12.9	972	12.0	1.4	2.9
29	2.3	2.5	36.4	ND	7.4	3.0	44.4	3.0	ND	20.1	908	23.6	2.5	3.7
30	2.7	3.9	53.1	ND	5.4	2.9	43.3	6.0	ND	25.4	858	17.2	2.9	3.1

ND: not detected

Table A22: Concentrations of trace metals (mg/kg) determined in sediments of the present study compared to other parts worldwide and along Alexandrian Coast.

Location	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Se	Sn	V	Zn	Reference
Abu Qir Bay (Present study)	0.23-11.0	0.082-3.54	0.727-22.8	4.66-186	0.95-127	0.241-2.7	2.05-40.5	2.71-129	0.342-4.00	1.32-12.1	5.8-129	5.77-717	Present study
Themaikos Gulf, Greece, 1981	NA	13-85	7.1-20	31-107	4-37	NA	35-160	13-228	NA	ND-3	NA	23-299	Chester and Voutsinou, 1981
Suruga Bay, Japan, 1993	NA	0.19-1.49	8.7-250	NA	32-414	NA	24-321	NA	NA	NA	70-214	89-147	Takemats et al. 1993
Wellington Harbour, New Zealand, 1996	8-26	NA	NA	61-84	13-80	NA	25-61	NA	NA	NA	NA	90-230	Dickinson et al. 1996
Coastal sediments, Greece, 1997	NA	NA	NA	NA	5.3-86.2	NA	NA	20.7-93	NA	0.03-0.44	NA	12.9-230	Angelidis and Aloupi, 1997
Tees Estuary, England, 1997	NA	2.6-9.8	16-56	36-577	25-262	NA	21-49	37-680	NA	NA	NA	65-777	Jones and Turki, 1997
La Coruna Estuary, Spain, 1997	1.29-9.93	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	Villa-Lojo et al. 1997
Boston Harbour, 1998	NA	NA	NA	93-179	44-99	NA	20-35	53-110	NA	NA	NA	86-160	Bothner et al. 1998
Aegean Sea, Greece, 2001	NA	0.03-0.495	NA	40-154	5.34-86.2	NA	NA	20.7-93.0	NA	NA	NA	12.9-230	Aloupi and Angelidis, 2001
Port Curtis Estuary, Australia, 2005	6-36	NA	NA	13-85	4-44	NA	4-33	23.8-89	NA	NA	NA	11-113	Jones et al. 2005

ND = not detected

( ): Values between brackets represent the average concentration

Table A22: Continued.

Station No.	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Se	Sn	V	Zn	Reference
Abu Qir Bay, 1980	NA	ND-14.12	NA	NA	ND-91	NA	NA	NA	NA	NA	NA	-7589	Saad et al. 1980
Abu Qir Bay, 1988	NA	NA	NA	NA	NA	NA	NA	NA	NA	(2.25)	NA	NA	Aboul Dahab, 1988
Abu Qir Bay, 1989	NA	NA	NA	48-368	NA	NA	NA	NA	NA	NA	NA	NA	Aboul Dahab, 1989
Abu Qir Bay, 1993	NA	NA	NA	NA	NA	NA	36.8-57.5	NA	NA	NA	50-91.7	NA	Abdel Moneim and Shata, 1993
Abu Qir Bay, 1993	NA	(5.8)	NA	350-760	115-210	(1.36)	NA	(229)	NA	NA	NA	215-500	EL-Sokkary, 1993
Abu Qir Bay, 2002	NA	0.21-0.62	NA	NA	NA	NA	NA	1.9-6.1	NA	NA	NA	NA	Aboul-Naga et al. 2002
Abu Qir Bay, 2006	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.78-5.36	NA	NA	Abdel-Fatah, 2006
Alexandria Coast, 1999	NA	NA	1.2-75.6	NA	NA	NA	NA	NA	NA	NA	NA	10.2-179.3	EL-Sammak and Aboul Kassim, 1999
Eastern Harbour, Alexandria, 2003	NA	NA	NA	NA	160.2-358.5	NA	NA	NA	NA	NA	NA	NA	Saad and Badr, 2003
Maadeya Sector	NA	NA	NA	NA	(150.83)	NA	NA	NA	NA	NA	NA	NA	
Tabia Sector	NA	NA	NA	NA	(193.76)	NA	NA	NA	NA	NA	NA	NA	
Western Harbour Alexandria, 2004	4.7-15	0.6-2.4	NA	26-649	27-378	NA	4.7-15	21-1070	0.4-2.4	1.9-22.4	NA	33-1221	Mostafa et al. 2004

( ): Values between brackets represent the average concentration.
NA: Not available

Table A23: Concentrations of trace metals (mg/kg dw) in mussel samples of Abu Qir Bay.

Station No.	As	Cd	Cr	Cu	Hg	Mn	Pb	Se	Zn
Mactra Corallina									
4	12.1	3.08	12.2	12.1	3.46	124	10.5	3.00	74.2
8	11.3	2.90	11.2	12.7	3.20	174	7.24	2.76	71.2
9	9.41	2.53	1.81	10.4	3.00	125	5.46	5.29	42.6
12	6.25	2.42	11.6	12.0	0.800	153	8.76	2.17	68.3
13	7.15	2.17	8.90	8.26	2.72	145	8.59	2.47	45.1
18	9.41	0.126	9.58	8.56	2.88	6.49	9.10	2.78	42.6
19	9.90	2.40	1.62	9.74	2.50	5.88	6.71	3.22	51.8
Min.	**6.25**	**0.126**	**1.62**	**8.26**	**0.800**	**5.46**	**5.46**	**2.17**	**42.2**
Max.	**12.1**	**3.08**	**12.2**	**12.7**	**3.46**	**10.5**	**10.5**	**5.29**	**74.2**
Mean	**9.36**	**2.23**	**8.13**	**10.5**	**2.65**	**8.05**	**8.05**	**3.10**	**56.5**
Sd	**2.09**	**0.980**	**4.53**	**1.78**	**0.874**	**1.69**	**1.69**	**1.02**	**14.2**
Tapes Decussata									
25	9.19	0.211	1.39	8.34	0.280	7.98	2.36	3.37	63.6
26	6.99	2.186	0.750	9.65	2.37	8.20	7.51	3.70	55.5
27	5.81	2.283	2.08	9.20	2.83	9.51	6.61	2.70	62.9
28	4.71	0.139	1.56	10.5	0.240	8.72	5.68	2.49	68.6
29	8.08	0.288	0.930	8.07	0.160	7.84	5.88	2.21	58.4
30	10.6	0.153	3.86	9.50	2.96	7.99	5.83	3.58	35.3
Min.	**4.71**	**0.139**	**0.750**	**8.07**	**0.160**	**7.84**	**2.36**	**2.21**	**35.3**
Max.	**10.6**	**2.28**	**3.86**	**10.5**	**2.96**	**9.51**	**7.51**	**3.70**	**68.6**
Mean	**7.56**	**0.877**	**1.76**	**9.21**	**1.47**	**8.37**	**5.65**	**3.01**	**57.4**
Sd	**2.18**	**1.05**	**1.13**	**0.891**	**1.38**	**0.637**	**1.75**	**0.622**	**11.7**

Table A24: Concentrations of trace metals (mg/kg dw) in different marine species worldwide.

Location	species	As	Cd	Cr	Cu	Hg	Mn	Pb	Se	Zn	Reference
Abu Qir Bay (Present study)	*Mactra corallina*	6.25-12.1	0.13-3.1	1.62-12.2	8.3-12.7	0.8-3.5	5.88-174	5.5-10.5	2.2-5.3	42.2-74.2	Present study
	Tapes decussata	4.7-10.6	0.14-2.28	0.75-3.86	8.1-10.5	0.16-2.96	7.84-9.51	2.36-7.51	2.21-3.7	35.3-68.6	
Mediterranean Sea	*Mactra corallina*	NA	0.001-<1	NA	>0.5-<2	0.001-<1	0.1-<30	NA	NA	>5-60	Herut et al. 1999
Algarve coast, Portugal	*Mytilus galloprovincialis*	NA	1.3-3.1	NA	4.8-7.0	NA	3.1-15.5	NA	NA	189-398	Machado et al. 1999
Bilbao estuary, Spain	*Scrobicularia plana*	NA	30-100	4.0-5.1	69-161	NA	10-18	87-198	NA	1704-4139	Ruiz and Salinas, 2000
Amurskii Bay, Russia	*Crenomytilus grayanus*	NA	3.2-14.3	NA	4.0-17	NA	NA	0.5-251	NA	83-270	Shulkin et al. 2002
Sepetiba Bay, Brazil	*Crassostrea rhizophorae*	NA	1.3-5.4	NA	NA	NA	NA	NA	NA	1628-28524	Rebelo et al. 2003
Qatar	*Clams*	156	1.17	0.97	8.35	0.32	17.7	1.45	7.15	69.1	De Mora et al. 2004
UAE	*Pearl Oyster*	16.2-37.7	2.73-9.97	0.29-2.36	5.1-63.8	0.01-0.1	8.4-25	0.15-2.3	2.69-5.71	159-1430	
Bahrain	*Pearl Oyster*	24.9-45.7	3.7-3.8	0.7-0.8	3.1-4.5	0.04-0.11	4.3-6.2	0.4-3.9	4.9-5.1	1825-4290	
Atlantic Coast, southern Spain	*Donax trunculus*	4.9-12.1	0.15-0.24	0.8-2.1	60-383	0.06-0.25	NA	1.1-9.5	NA	56-152	Usero et al. 2005
Port Curtis, Australia	*Oyster*	3.3-6.9	0.14-0.42	0.2-9.4	114-363	0.03-0.09	NA	<0.04-0.09	0.3-1.5	463-1400	Jones et al. 2005
McMurdo Sound, Antarctica	*L. elliptica*	10-66	5-57	NA	4.2-543	0.1-21	NA	0.3-6.7	NA	48-419	Negri et al. 2006
Naboc River, Philippines	*Taiwan clam*	NA	(0.12)	NA	NA	0.233-0.544	NA	(0.22)	NA	NA	Appelton et al. 2006

( ): Values between brackets represent the average concentration.
NA: Not available

Table A24: Continued.

Location	species	As	Cd	Cr	Cu	Hg	Mn	Pb	Se	Zn	Reference
Abu Qir Bay	*Mactra corallina*	6.25-12.1	0.13-3.1	1.62-12.2	8.3-12.7	0.8-3.5	5.88-174	5.5-10.5	2.2-5.3	42.2-74.2	Present study
	Tapes decussata	4.7-10.6	0.14-2.28	0.75-3.86	8.1-10.5	0.16-2.96	7.84-9.51	2.36-7.51	2.21-3.7	35.3-68.6	
Alexandrian Coast											
1- Fish species											
Abu Qir Bay	*Mullus Barbatus*	NA	NA	NA	NA	0.13-0.346 *	NA	NA	NA	NA	Emara, 1982
Abu Qir Bay	*Pagellus erythrinus*	(4.1)	(0.023)	NA	(6.9)	0.62	NA	(0.47)	NA	(16.5)	EL-Nabawi et al. 1987a
EL-Mex Bay	*Sparus auratus*	NA	(0.3)	NA	(0.3)	NA	(0.5)	(0.5)	NA	NA	Abd *Allah* et al. 2001
2- Algal species											
EL-Mex Bay	*Ulva lactuca*	NA	(0.92)	NA	(10.7)	(0.1)	(33)	(14.2)	NA	(18.2)	Mohamed and Khaled, 2007
	Corallina mediterranea	NA	(7.2)	NA	(8.1)	(0.19)	(49.2)	(26.5)	NA	(53)	
Eastern Harbour	*Ulva lactuca*	NA	(1.1)	NA	(26.1)	(1.2)	(12.6)	(9.4)	NA	(50.4)	
	Corallina mediterranea	NA	(10)	NA	(16.7)	(2.4)	(21.1)	(53.3)	NA	(60.5)	
Abu Qir Bay	*Ulva lactuca*	NA	(0.45)	NA	(5.6)	(1.2)	(28.8)	(17.1)	NA	(8)	
	Corallina mediterranea	NA	(11.1)	NA	(4.7)	(1.5)	(36.2)	(49.4)	NA	(13.4)	
3- Bivalves											
EL-Mex Bay	*Donax trunculus*	NA	0.12-0.96	NA	NA	0.5-1.1	NA	0.02-0.16	NA	NA	Aboul-Dahab, 1985
	Mactra corallina	NA	0.12-0.98	NA	NA	0.3-0.9	NA	0.03-0.25	NA	NA	

( ): Values between brackets represent the average concentration.
NA: not available

Table A24: Continued.

Location	Species type	As	Cd	Cr	Cu	Hg	Mn	Pb	Se	Zn	Reference
Abu Qir Bay	*Mactra corallina*	6.25-12.1	0.13-3.1	1.62-12.2	8.3-12.7	0.8-3.5	5.88-174	5.5-10.5	2.2-5.3	42.2-74.2	Present study
	Tapes decussata	4.7-10.6	0.14-2.28	0.75-3.86	8.1-10.5	0.16-2.96	7.84-9.51	2.36-7.51	2.21-3.7	35.3-68.6	
Alexandrian Coast											
EL-Mex Bay	*Mytilus minimus*	NA	NA	NA	NA	NA	NA	(0.3)	(0.03)	NA	Abdel-Moati and Atta, 1991
EL-Mex Bay	*Mytilus* spp.	NA	NA	NA	NA	(1.98)	NA	(8.3)	NA	NA	Abdel-Moati, 1991
Abu Qir Bay	*Mytilus* spp.	NA	NA	NA	NA	(0.49)	NA	(6.3)	NA	NA	Abdel-Moati, 1991
Abu Qir Bay	*Donax trunculus*	NA	(2.66)	NA	(7.94)	NA	NA	(2.48)	NA	(26.7)	Khalid, 1997
Abu Qir Bay	*Mactra corallina*	NA	(2.2)	NA	(6.1)	NA	NA	(2.25)	NA	(19.4)	EL-Rayis et al. 1997
Abu Qir Bay	*Donax trunculus*	NA	(3.56)	NA	NA	NA	NA	(2.67)	NA	NA	Ahdy, 1999
	Mactra corallina	NA	(2.82)	NA	NA	NA	NA	(2.24)	NA	NA	
Abu Qir Bay	*Donax trunculus*	NA	4.4-4.88	NA	NA	NA	NA	1.67-1.89	NA	NA	Abdel-Moati, 2002
Abu Qir Bay	*Donax trunculus*	NA	0.15-0.39	NA	4.07-10.2	NA	6.12-6.92	0.86-0.93	NA	11.02-15.0	EL-Sikaily et al. 2004

( ): Values between brackets represent the average concentration.
NA: not available

Table A25: Concentrations of PCBs (µg/kg dw) in surfacial sediments of Abu Qir Bay.

Station No.	PCB 28	PCB 52	PCB 70	PCB 101	PCB 118	PCB 153	PCB 138	PCB 126	PCB 156	PCB 180	PCB 169	Σ11 PCBs	Σ6 PCBs
1	0.907	0.744	2.80	2.14	3.27	2.85	3.92	0.432	0.881	1.50	1.10	20.5	12.1
2	1.04	1.15	4.76	3.13	3.08	2.33	2.85	0.516	1.13	1.57	0.615	22.2	12.1
3	<DL	<DL	<DL	<DL	<DL	<DL	0.356	<DL	<DL	0.557	<DL	0.913	0.913
4	0.807	0.593	2.95	2.26	2.81	1.72	1.54	0.550	0.525	1.23	<DL	15.0	8.14
5	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
8	<DL	0.309	1.51	1.08	1.42	0.846	0.853	<DL	<DL	<DL	<DL	6.01	3.09
9	<DL	<DL	<DL	<DL	<DL	0.337	<DL	<DL	<DL	0.457	<DL	0.794	0.794
12	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
13	0.292	<DL	0.555	<DL	<DL	0.564	<DL	<DL	<DL	0.513	<DL	1.92	1.37
14	0.270	<DL	1.36	0.833	1.10	1.44	1.51	<DL	0.957	0.440	1.28	9.21	4.50
15	<DL	<DL	<DL	<DL	<DL	0.246	0.147	<DL	<DL	0.127	<DL	0.520	0.520
18	<DL	<DL	0.757	0.393	0.947	0.395	0.627	<DL	<DL	0.113	<DL	3.23	1.53
19	0.499	0.341	1.64	1.08	1.15	1.13	0.656	<DL	<DL	0.757	<DL	7.25	4.46
20	0.472	0.426	2.35	1.44	2.32	2.23	2.12	0.361	0.452	0.914	<DL	13.1	7.61
21	0.382	0.308	2.57	1.65	<DL	2.23	1.19	<DL	0.253	1.13	<DL	9.71	6.88
22	0.368	0.217	0.900	0.521	0.461	0.311	0.126	<DL	<DL	0.114	<DL	3.02	1.66
23	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
25	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
26	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
27	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Min	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**
Max	**1.04**	**1.15**	**4.76**	**3.13**	**3.27**	**2.85**	**3.92**	**0.550**	**1.13**	**1.57**	**1.28**	**22.2**	**12.1**
Mean	**0.252**	**0.205**	**1.11**	**0.726**	**0.828**	**0.838**	**0.798**	**0.093**	**0.210**	**0.476**	**0.150**	**5.68**	**3.28**
Sd	**0.340**	**0.319**	**1.36**	**0.951**	**1.16**	**0.953**	**1.10**	**0.194**	**0.372**	**0.534**	**0.383**	**7.10**	**4.01**

<DL = below the limit of detection

Table A26: Concentrations of PCBs (µg/kg dw) in mussel tissues of Abu Qir Bay.

Station No.	PCB 28	PCB 52	PCB 70	PCB 101	PCB 118	PCB 153	PCB 138	PCB 126	PCB 156	PCB 180	PCB 169	Σ11 PCBs	Lipid %
Mactra corallina													
4	11.1	7.16	20.0	14.5	26.4	7.91	12.6	2.00	2.36	3.03	<DL	107	5.17
8	6.25	3.95	11.1	12.2	14.8	5.05	7.38	<DL	0.657	1.45	<DL	62.8	4.79
9	<DL	<DL	<DL	<DL	<DL	0.454	0.288	<DL	<DL	0.218	<DL	0.960	4.28
12	<DL	<DL	<DL	<DL	0.316	0.935	0.902	<DL	<DL	<DL	<DL	2.15	4.06
13	<DL	<DL	0.537	5.20	0.539	1.40	1.37	<DL	<DL	<DL	<DL	9.06	4.26
18	5.20	3.12	9.36	7.01	12.8	4.08	5.76	0.666	0.324	<DL	<DL	48.4	4.64
19	4.86	3.69	13.2	11.2	21.3	7.02	9.43	0.770	1.32	0.577	<DL	73.3	4.83
Min	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**0.454**	**0.288**	**<DL**	**<DL**	**<DL**		**0.960**	
Max	**11.1**	**7.16**	**20.0**	**14.5**	**26.4**	**7.91**	**12.6**	**2.00**	**2.36**	**3.03**		**107**	
Mean	**3.91**	**2.56**	**7.74**	**7.15**	**10.9**	**3.84**	**5.40**	**0.490**	**0.666**	**0.754**		**43.4**	
Sd	**4.19**	**2.72**	**7.80**	**5.80**	**10.8**	**3.00**	**4.75**	**0.746**	**0.889**	**1.13**		**40.9**	
Tapes decussata													
25	0.936	<DL	0.296	<DL	<DL	0.961	0.435	<DL	<DL	0.691	<DL	3.32	8.19
26	0.543	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.543	7.99
27	1.78	<DL	<DL	2.20	<DL	2.48	1.94	<DL	<DL	1.68	<DL	10.1	8.83
Min	**0.543**		**<DL**	**<DL**		**<DL**	**<DL**			**<DL**		**0.543**	
Max	**1.78**		**0.296**	**2.20**		**2.48**	**1.94**			**1.68**		**10.1**	
Mean	**1.09**		**0.099**	**0.734**		**1.15**	**0.792**			**0.790**		**4.65**	
Sd	**0.631**		**0.171**	**1.27**		**1.25**	**1.02**			**0.843**		**4.91**	

<DL = below the limit of detection

Table A27: Concentrations of DDTs and its metabolites DDD and DDE and HCH isomers (µg/kg dw) in surfacial sediments of Abu Qir Bay.

Sample No.	o,p'-DDT	o,p'-DDD	o,p'-DDE	p,p'-DDT	p,p'-DDD	p,p'-DDE	DDTs	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCH
1	<DL	37.6	15.5	7.95	40.8	26.1	128	7.95	4.03	21.5	1.03	34.5
2	<DL	32.0	0.397	6.48	44.5	32.5	116	3.77	12.3	11.3	2.53	29.9
3	<DL	0.578	<DL	<DL	<DL	0.829	1.41	<DL	<DL	<DL	<DL	<DL
4	5.45	26.4	0.655	3.82	17.7	10.1	64.2	8.72	<DL	7.77	2.23	18.7
5	<DL	<DL	<DL	<DL	<DL	0.211	0.211	<DL	<DL	<DL	<DL	<DL
8	<DL	5.12	<DL	<DL	8.05	3.31	16.5	0.871	<DL	1.26	0.462	2.59
9	<DL	0.181	<DL	<DL	0.675	0.264	1.12	<DL	<DL	0.324	<DL	0.324
12	0.441	7.70	<DL	1.22	8.82	2.88	21.1	0.857	<DL	1.54	0.703	3.10
13	0.604	1.01	<DL	<DL	0.408	0.306	2.33	<DL	<DL	0.187	0.175	0.362
14	0.686	4.79	0.371	<DL	2.93	3.09	11.9	2.19	0.790	1.92	0.896	5.79
15	<DL	2.72	<DL	0.190	3.63	1.78	8.32	<DL	<DL	1.27	0.388	1.66
18	<DL	1.07	<DL	2.56	0.698	0.905	5.23	<DL	<DL	0.300	<DL	0.300
19	<DL	2.84	<DL	0.480	12.5	6.00	21.8	0.270	<DL	0.948	0.840	2.06
20	<DL	12.6	0.624	<DL	21.4	7.56	42.2	10.4	1.21	11.0	0.701	23.2
21	<DL	20.6	17.0	<DL	24.8	19.6	82.0	7.87	2.94	13.4	1.88	26.1
22	<DL	0.956	<DL	<DL	1.49	1.01	3.46	0.237	<DL	0.244	<DL	0.481
23	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
25	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
26	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.402	<DL	<DL	0.402
27	0.642	0.738	<DL	3.18	<DL	0.584	5.14	1.05	<DL	<DL	0.543	1.59
Min	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**
Max	**5.45**	**38.0**	**17.0**	**7.95**	**44.5**	**32.5**	**128**	**10.4**	**12.3**	**21.5**	**2.53**	**34.5**
Mean	**0.391**	**7.84**	**1.73**	**1.29**	**9.42**	**5.85**	**26.5**	**2.21**	**1.08**	**3.65**	**0.619**	**7.56**
Sd	**1.21**	**11.7**	**4.99**	**2.35**	**13.7**	**9.37**	**39.6**	**3.50**	**2.85**	**6.04**	**0.779**	**11.6**

<DL = below the limit of detection

Table A28: Concentrations of cyclodienes (µg/kg dw) in surfacial sediments of Abu Qir Bay.

Sample No.	Cis-chlordane	Trans-chlordane	Σchlordane	Heptachlor	Cis-epoxide	Trans-epoxide	Aldrin	Dieldrin	α-endosulfane	β -endosulfane	Mirex
1	15.4	24.2	39.6	2.72	1.84	9.92	9.92	18.3	8.35	4.84	<DL
2	13.2	27.1	40.3	2.19	3.44	8.31	8.31	11.5	6.95	5.44	<DL
3	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
4	5.92	22.4	28.4	<DL	0.881	7.25	7.25	<DL	6.74	3.81	<DL
5	<DL	<DL	<DL	<DL	0.092	<DL	<DL	<DL	<DL	<DL	<DL
8	1.41	3.86	5.27	<DL	0.264	1.44	1.44	4.62	1.88	1.56	0.299
9	0.353	0.614	0.967	<DL	0.210	<DL	<DL	<DL	0.326	<DL	<DL
12	3.04	3.49	6.53	<DL	0.281	2.71	2.71	4.46	<DL	1.30	0.209
13	0.422	0.389	0.810	0.278	<DL	<DL	<DL	0.302	0.153	0.626	<DL
14	2.04	4.11	6.16	<DL	<DL	1.44	1.44	3.93	1.48	0.531	0.337
15	1.33	2.42	3.75	<DL	<DL	0.999	0.999	1.68	1.30	0.800	<DL
18	2.23	2.77	5.00	<DL	<DL	<DL	<DL	0.623	0.107	0.405	<DL
19	6.51	2.55	9.06	<DL	<DL	5.87	5.87	<DL	0.972	0.500	<DL
20	7.98	12.4	20.3	4.41	2.60	<DL	<DL	14.8	6.88	3.44	0.824
21	8.22	13.3	21.5	1.68	3.74	<DL	<DL	10.6	9.45	5.46	0.356
22	0.625	0.786	1.41	<DL	<DL	0.744	0.744	1.73	0.542	0.606	<DL
23	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
25	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
26	0.466	<DL	0.466	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
27	0.751	<DL	0.751	<DL	<DL	<DL	<DL	0.647	0.518	<DL	<DL
Min	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**
Max	**15.4**	**27.1**	**40.3**	**4.41**	**3.74**	**9.92**	**9.92**	**18.3**	**9.45**	**5.46**	**0.824**
Mean	**3.50**	**6.02**	**9.52**	**0.564**	**0.668**	**1.93**	**1.93**	**3.66**	**2.28**	**1.47**	**0.106**
Sd	**4.58**	**8.87**	**13.2**	**1.22**	**1.22**	**3.18**	**3.18**	**5.60**	**3.28**	**1.95**	**0.210**

<DL = below the limit of detection

Table A29: Concentrations of methoxychlor, chlorpyrifos, PCBz and HCBz (µg/kg dw) in surfacial sediments of Abu Qir Bay.

Sample No.	Methoxychlor	Chlorpyrifos	PCBz	HCBz
1	<DL	29.6	0.394	0.199
2	<DL	41.8	0.584	0.128
3	<DL	<DL	<DL	<DL
4	5.16	17.4	5.73	22.0
5	<DL	0.496	<DL	<DL
8	<DL	1.06	<DL	<DL
9	<DL	0.639	<DL	<DL
12	<DL	<DL	<DL	<DL
13	<DL	0.471	<DL	<DL
14	1.57	1.22	<DL	<DL
15	1.29	<DL	<DL	<DL
18	1.92	<DL	<DL	<DL
19	<DL	6.05	4.72	4.85
20	<DL	8.06	0.085	<DL
21	<DL	8.81	<DL	0.167
22	<DL	2.69	<DL	<DL
23	<DL	<DL	<DL	<DL
25	<DL	0.200	<DL	<DL
26	<DL	<DL	<DL	<DL
27	<DL	<DL	<DL	<DL
Min	**<DL**	**<DL**	**<DL**	**<DL**
Max	**5.16**	**41.8**	**5.73**	**22.0**
Mean	**0.555**	**5.92**	**0.576**	**1.37**
Sd	**1.25**	**11.3**	**1.61**	**4.98**

<DL = below the limit of detection

Table A30: Comparison of PCBs and organochlorine pesticide concentrations (µg/kg dw) in surfacial sediments of Abu Qir Bay with concentrations worldwide.

Location	Sampling year	PCBs	DDTs	HCHs	Chlordanes	Aldrin	Dieldrin	References
Abu Qir Bay, Egypt	2006	<DL-22.2	<DL-128	<DL-34.5	<DL-54.6	<DL-9.32	<DL-19.2	Present study
San Francisco Bay-Delta Estuary	1992	NA	<0.1-8.8	NA	<0.1-1.5	NA	NA	Periera et al. 1994
Casco Bay, Maine, USA	1991	0.4-485	<0.2-20	<DL-0.48	<DL-4.91	NA	NA	Kennicutt et al. 1994
Northwest Basin, Mediterranean Sea	1990	1.4-5.8	1.2-5.8	NA	NA	NA	NA	Tolosa et al. 1995
Barcelona Offshore, Spain	1990	4.0-64	4.9-79.0	NA	NA	NA	NA	Tolosa et al. 1995
Rhone Prodelta, France	1990	38-230	73-704	NA	NA	NA	NA	Tolosa et al. 1995
Mediterranean sediments, France	NA	29-181	NA	NA	NA	NA	NA	Pierad et al. 1996
Western Baltic Sea	1993	<DL-11.4	<DL-9.0	<DL-1.0	NA	NA	NA	Dannenberger, 1996
San Francisco Bay, California, USA	1993	NA	11-30212	NA	0.5-150	NA	<DL-400	Periera et al. 1996
Arabian Sea, West Coast of India	NA	NA	1.5-25.2	0.85-7.87	NA	0.1-0.27	0.7-3.33	Sarkar et al. 1997
Ho Chi Minh City´s Canals, Vietnam	1996	<DL-123	1.8-254		NA	NA	NA	Phuong et al. 1998
North Baltic Sea, Sweeden	1992	9.0-9.3	1.9-6.9	0.79	0.57	NA	0.51	Strandberg et al. 1998
Clyde Estuary, UK	NA	0.5-1822	NA	NA	NA	NA	NA	Edgar et al. 1999
Da-han River, Taiwan	1998	NA	<DL-3.89	<DL-2.5	NA	<DL-5.8	<DL-0.56	Doong et al. 2002
Tonghui River, Beijing, China	2002	0.78-8.47	0.11-3.78	0.06-0.38	NA	<DL-0.08	<DL-8.83	Zhang et al. 2004
Amur Bay, Russia	2001	NA	1.7-16.3	0.2-0.8	NA	NA	NA	Vashchenko et al. 2005
Saronikos Gulf, Greece	1998	41800-351800	9100-75600	100-300	NA	NA	NA	Galanopoulou et al. 2005
Danube Delta, Romania	2001	<DL	0.9-17	0.9-6.8	NA	NA	NA	Covaci et al. 2006
Mediterranean Sea sediments	NA	0.03-3938	0.003-75600	NA	NA	NA	NA	Guitierrez et al. 2007
Inner Clyde Estuary, UK	2003	5.2-130	NA	NA	NA	NA	NA	Vane et al. 2007
Ariake Bay, Japan	2005	NA	1.0-1.5	0.78-1.5	0.38-0.4	<DL-0.01	0.01-0.15	Kim et al. 2007
Lake Mariut, Egypt	NA	NA	318-982[b]	52.8-143[c]	NA	NA	NA	Abo-Elamayem et al. 1979
Nile Delta, Egypt	NA	NA	NA	NA	0.2-12	0.1-59	NA	Abdallah et al. 1992
Abu Qir Bay, Egypt	1989	53-231[a]	44-223	16-82	11.0-45.0	13-72	<0.1-5.0	Abdallah and Abbas, 1994
EL-Mex Bay, Egypt	1989	68-164[a]	32.3-87	16-53	NA	NA	NA	Abdallah and Abbas, 1994
Alexandria Harbour, Egypt	1998	0.9-1210	<0.25-885	0.25-6	<0.25-44	<DL-4.6	<DL-3.1	Barakat et al. 2002

<DL = below the limit of detection a: PCB calculated as aroclor equivalents b: DDTs calculated as p,p´DDT
c: HCHs calculated as lindane Chlordanes: sum of cis and trans chlordane, heptachlor and its epoxides NA: not available

Table A30: Continued.

Location	Sampling year	Chlorpyrifos	Endosulfane	PCBz	HCBz	Methoxychlor	Mirex	References
Abu Qir Bay, Egypt	2006	<DL-41.8	<DL-16.9	<DL-5.7	<DL-22.0	<DL-5.16	<DL-0.6	Present work
San Francisco Bay-Delta Estuary	1992	NA	NA	<0.1-3.2	<0.1-3.4	NA	NA	Periera et al. 1994
Western Baltic Sea	1993	NA	NA	NA	<DL-0.750	NA	NA	Dannenberger, 1996
Da-han River, Taiwan	1998	NA	<DL-5.98	NA	NA	<DL-2.85	NA	Doong et al. 2002
Alexandria Harbour, Egypt	1998	<DL-51	<DL-22	NA	NA	NA	<DL-0.4	Barakat et al. 2002

<DL = below the limit of detection
NA: not available

Table A31: Concentrations of organochlorine pesticides in mussel tissues of Abu Qir Bay.

Sample No.	o,p'-DDE	o,p'-DDD	p,p'-DDE	p,p'-DDD	DDTs	Cis-chlord.	Trans-chlord.	ΣChlord	Chlorpyr	Dieldrin	Mirex	PCBz
Mactra corallina												
4	0.877	5.81	13.1	6.34	26.1	16.8	14.9	31.7	9.95	11.5	<DL	0.328
8	3.61	5.52	14.0	8.21	31.3	2.91	11.5	14.4	13.9	2.57	<DL	0.393
9	<DL	0.380	2.57	1.99	4.94	<DL	1.08	1.08	3.30	<DL	<DL	<DL
12	<DL	0.370	3.32	2.45	6.14	<DL	0.910	0.910	4.63	2.44	0.891	<DL
13	<DL	0.410	3.80	2.79	7.00	<DL	1.30	1.30	6.83	2.86	<DL	<DL
18	1.10	5.07	7.07	3.55	16.8	<DL	10.3	10.3	15.0	<DL	<DL	<DL
19	<DL	1.65	3.28	1.62	6.55	<DL	2.87	2.87	3.26	<DL	0.461	<DL
Min	**<DL**	**0.37**	**2.57**	**1.62**	**4.94**	**<DL**	**0.910**	**0.910**	**3.26**	**<DL**	**<DL**	**<DL**
Max	**3.61**	**5.81**	**14.0**	**8.21**	**31.3**	**16.8**	**14.9**	**31.7**	**15.0**	**11.5**	**0.891**	**0.393**
Mean	**0.798**	**2.74**	**6.73**	**3.85**	**14.1**	**2.82**	**6.11**	**8.93**	**8.13**	**2.77**	**0.193**	**0.103**
Sd	**1.33**	**2.59**	**4.88**	**2.48**	**10.8**	**6.27**	**5.90**	**11.3**	**4.92**	**4.07**	**0.352**	**0.177**
Tapes decussata												
25	<DL	<DL	1.45	0.440	1.89	<DL	<DL	<DL	<DL	<DL	<DL	<DL
26	<DL	<DL	0.944	<DL	0.944	<DL	<DL	<DL	<DL	<DL	<DL	<DL
27	<DL	<DL	3.14	1.27	4.41	<DL	<DL	<DL	0.327	<DL	<DL	<DL
Min			**0.944**	**<DL**	**0.944**				**<DL**			
Max			**3.14**	**1.27**	**4.41**				**0.327**			
Mean			**1.84**	**0.570**	**2.41**				**0.109**			
Sd			**1.15**	**0.645**	**1.79**				**0.189**			

<DL = below the limit of detection

Table A31: Continued.

Sample No.	α-HCH	γ-HCH	δ-HCH	HCHs	α-endosulfane	β-endosulfane	Endosulfane	Heptachlor	Cis-epoxide	Trans-epoxide	Methoxychlor	HCBz
Mactra corallina												
4	3.58	6.72	0.62	10.9	6.32	2.94	9.26	1.48	0.466	1.06	4.02	0.499
8	4.09	3.97	<DL	8.06	4.27	<DL	4.27	1.00	<DL	<DL	1.30	0.391
9	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
12	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
13	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.968	<DL	0.458
18	2.74	2.76	1.00	6.50	<DL	<DL	<DL	1.00	0.551	1.65	2.87	<DL
19	0.745	1.36	<DL	2.11	<DL	0.632	0.632	<DL	0.381	1.15	<DL	<DL
Min	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**
Max	**4.09**	**6.72**	**1.00**	**10.9**	**6.32**	**2.94**	**9.26**	**1.48**	**0.551**	**1.65**	**4.02**	**0.499**
Mean	**1.59**	**2.12**	**0.231**	**3.94**	**1.51**	**0.510**	**2.02**	**0.498**	**0.200**	**0.690**	**1.17**	**0.193**
Sd	**1.82**	**2.55**	**0.410**	**4.51**	**2.65**	**1.10**	**3.55**	**0.641**	**0.254**	**0.680**	**1.66**	**0.242**
Tapes decussata												
25	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.392
26	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
27	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.362	<DL	<DL	<DL	0.400
Min								**<DL**				**<DL**
Max								**0.362**				**0.400**
Mean								**0.121**				**0.264**
Sd								**0.209**				**0.229**

<DL = below the limit of detection

Table A32: Concentrations of chlorinated organic compounds (µg/kg) in different marine species worldwide.

Location	Sampling year	Species type	PCBs	ΣDDT	HCHs	HCBz	Endosulfane	Heptachlor	Reference
Abu Qir Bay	2006	*Mactra corallina*	0.96-107[x] (43.4)	4.94-31.3[x] (14.1)	<DL-10.9[x] (3.94)	<DL-0.499[x] (0.193)	0.137-11.3[x] (2.80)	<DL-1.48[x] (0.498)	Present study
			22.4-2071[y] (887)	115-645[y] (296)	<DL-211[y] (80.4)	<DL-9.87[y] (3.95)	3.2-219[y] (56.9)	<DL-28.6[y] (10.2)	
			0.21-19.9[z] (7.97)	1.1-5.4[z] (2.6)	<DL-2.03[z] (0.721)	<DL-0.093[z] (0.035)	0.03-2.2[z] (0.515)	<DL-0.275[z] (0.091)	
		Tapes decussata	0.54-10.1[x] (4.65)	0.944-4.41[x] (2.41)	ND	<DL-0.399[x] (0.264)	ND	<DL-0.362[x] (0.120)	
			6.79-114[y] (53.8)	11.8-49.9[y] (28.3)	ND	<DL-4.79[y] (3.11)	ND	<DL-4.10[y] (1.37)	
			0.1-1.82[z] (0.85)	0.182-0.798[z] (0.445)	ND	<DL-0.073[z] (0.049)	ND	<DL-0.066[z] (0.022)	
1- Fish and crab worldwide									
Israel Coast	NA	*Mullus barbatus*	70[z]	NA	NA	NA	NA	NA	Ravid et al. 1985
Catalonia	NA	*Mullus barbatus*	200-8700[z]	NA	NA	NA	NA	NA	Albaiges et al. 1987
Hudson River, USA	1994-1995	*Striped bass*	500-4000[ez]	NA	NA	NA	NA	NA	Ashley et al. 2000
Salton Sea Lake, CA, USA	2001	*Tilapia mossambique*	10.1-115[dz]	6.8-216[z]	<0.1-1.7[z**]	1.0-72.4[z]	0.5-20.4[z]	NA	Sapozhinkova et al. 2004
Bahrain coastal region	2000-2001	Fish (muscle)	2.39-40.1[fx]	NA	NA	NA	NA	NA	De Mora et al. 2005
Coasts of Brittany and Normandy, France	2003	*Cancer Pagurus*	52-617[bx]	2.2-11.6[x*]	NA	0.28-0.46[x]	NA	NA	Bodin et al. 2007
Hudson Ship Channel, USA	2002-2003	Catfish	2.2-866[gz]	NA	NA	NA	NA	NA	Howell et al. 2008

a: sum of 20 congeners b: sum of 16 congeners c: sum of 7 congeners d: sum of 55 PCB congeners e: sum of 209 congeners
f: sum of 15 congeners g: 18 NOAA congeners h: sum of 24 congeners *: DDTs given as p,p´DDE **: HCHs given as lindane
x: concentrations are given on dry weight basis y: concentrations are given lipid based z: concentrations are given on wet weight basis
( ): values between brackets represent average concentration NA: not available

Table A32: Continued.

Location	Sampling year	Species type	PCBs	ΣDDT	HCHs	HCBz	Endosulfane	Heptachlor	Reference
1- Mussels worldwide									
Mediterranean Sea	NA	*Mytilus galloprovincialis*	0.9-97.2[z]	NA	NA	NA	NA	NA	Porte et al. 1988
Alfacs Bay, Spain	1991	*Mytilus galloprovincialis*	9.7[z]	7.5[z]	0.1[z]	0.6[z]	NA	NA	Sole et al. 1994
Fangar Bay, Spain	1992		6.0[z]	1.1[z]	ND	ND	NA	NA	
Catalonia	NA	*Mytilus galloprovincialis*	13.1-51.1[z]	NA	NA	NA	NA	NA	Porte and Albaiges, 1994
San Joaquin River, California	1992	*Corbicula fluminea*	NA	15-4350[x]	NA	NA	NA	NA	Pereira et al. 1996
Venice Lagoon, Italy	NA	Mussels	NA	0.2-2.7[z]	NA	NA	NA	NA	Di Domenico et al. 1997
Coastal Zone of Kenya	1992	*Venus* sp.	7.4-165[cy]	1.9-31.3[y*]	NA	NA	NA	NA	Everaarts et al. 1998
		Anadara sp.	20-336[cy]	15.1-47.8[y*]	NA	NA	NA	NA	
		Mactra sp.	9.7[cy]	2.4[y*]	NA	NA	NA	NA	
Arcachon Bay, France	1997	*Mytilus edulis*	33.9[ax]	23.4[x]	NA	NA	NA	NA	Thompson et al. 1999
Baltic Sea, Danish Sounds	1989	*Mytilus edulis*	38-3300[y]	29-2980[y]	53-770[y]	NA	NA	NA	Gustavson and Jonsson, 1999
Ebro Delta, NW Mediterranean	1989-1991	*Mytilus galloprovincialis*	7-70[z]	2-144[z]	NA	NA	NA	NA	Sole et al. 2000
		Ostrea edulis	5-38[z]	3-66[z]	NA	NA	NA	NA	
		Crassostrea gigas	8-30[z]	10-104[z]	NA	NA	NA	NA	
		Rotala decussata	1-18[z]	0.6-7[z]	NA	NA	NA	NA	
Guanabara Bay, Brazil	1996	*Perna perna*	NA	6.82-64.0[x]	0.81-5.9[x**]	0.0002-4.59[x]	NA	NA	De Brito et al. 2002
Pearl River Delta, China	1996	*Perna viridis*	82.8-615[y]	9.5-191[y]	ND-1.1[y]	NA	NA	NA	Fu et al. 2003
Adriatic Sea, Italy	NA	*Mytilus galloprovincialis*	ND-20.3[z]	ND-6.63[z]	NA	ND-0.5[z]	NA	NA	Marcotrigiano and Storelli, 2003
Bay of Fundy, Atlantic Canada	NA	*Mytilus edulis*	ND-38.2[hx]	NA	NA	NA	NA	NA	Chou et al. 2003
Monterey Harbour, California, USA	1999	Mussel	15.8[z]	11.5[z]	0.99[z]	NA	NA	NA	Kannan et al. 2004

Table A32: Continued.

Location	Sampling year	Species type	PCBs	ΣDDT	HCHs	HCBz	Endosulfane	Heptachlor	Reference
Danube Delta, Romania	2001	*Chironomus plumosus*	8.9-10.0[x]	26-39[x]	29-83[x]	<0.2-0.4[x]	NA	NA	Covaci et al. 2006
River Nestos, Greece	2004	*L. cephalus*	4.40-4.97[z]	ND-0.40[z]	0.10-0.27[z]	NA	NA	NA	Christoforidis et al. 2008
2- Fish along the Egyptian Coast									
Mediterranean Sea, Port Said, Egypt	1983	*Solea vulgaris*	125-1168[x]	56.5-148[x]	14.7-28.2[x**]	0.1-63.5[x]	NA	NA	EL-Dib and Badawy, 1985
Abu Qir Bay, Egypt (Fish)	1985	*Pagellus erythrinus*	47.3-77.2[z]	58.7-119[z]	20.7-25.5[z]	1.3-4.5[z]	NA	4.5-5.3[z]	EL-Nabawi et al. 1987b
		Sargus vulgaris	80.3-89.5[z]	12.9-150[z]	7.6-16.0[z]	4.2-4.8[z]	NA	2.8-3.9[z]	
		Siganus rivulatus	60.9-71.5[z]	129-157[z]	24.4-34.9[z]	5.9-7.8[z]	NA	1.8-2.8[z]	
		Sphyraena sphyraena	66.9-73.9[z]	67.3-109[z]	26.6-38.4[z]	2.8-5.9[z]	NA	1.3-2.6[z]	
		Trigla hirundo	25.7-55.6[z]	54.0-113[z]	14.9-23.8[z]	2.2-5.2[z]	NA	0.6-1.9[z]	
Lake Maryut	NA	Fish	NA	NA	NA	NA	NA	0.2-0.6[z]	Abd-Allah and Ali, 1994
Fish from the Egyptian Market	NA	*Tilapia nilotica*	NA	NA	NA	NA	NA	398[z]	Dogheim et al. 1996b
Abu Qir Bay, Egypt	NA	*Mugil sephalus*	30.8[z]	3.5[z]	NA	2.7[z]	3.6[z]	ND	Abd-Allah et al. 1998
Nile River and Manzala Lake	1993	*Tilapia nilotica*	NA	NA	NA	NA	NA	0.07-0.16[z]	Yamashita et al. 2000
3- Mussels along the Egyptian Coast									
Abu Qir Bay, Egypt		*Donax trunculus*	37.0[z]	22.4[z]	NA	2.1[z]	1.1[z]	ND	Abd-Allah et al. 1998

NA: not available
ND: Not detected

Table A32: Continued.

Location	Sampling year	Species type	Chlorpyrifos	Dieldrin	∑CHLs	Heptachlor epoxide	Methoxychlor	Mirex	Reference
Abu Qir Bay	2006	*Mactra corallina*	3.26-15.0[x] (8.13)	<DL-11.5[x] (2.77)	0.91-31.7[x] (8.93)	<DL-2.20[x] (0.890)	<DL-4.02[x] (1.17)	<DL-0.891[x] (0.193)	Present study
			67.6-323[y] (173)	<DL-222[y] (56.8)	22.4-613[y] (181)	<DL-47.4[y] (18.5)	<DL-77.7[y] (23.8)	<DL-21.9[y] (4.5)	
			0.601-2.85[z] (1.51)	<DL-2.14[z] (0.510)	0.167-5.90[z] (1.64)	<DL-0.418[z] (0.167)	<DL-0.75[z] (0.217)	<DL-0.164[z] (0.036)	
		Tapes decussata	<DL-0.327[x] (0.109)	ND	ND	ND	ND	ND	
			<DL-3.7[y] (1.23)	ND	ND	ND	ND	ND	
			<DL-0.059[z] (0.02)	ND	ND	ND	ND	ND	
1- Mussels worldwide									
San Joaquin River, California	1992	*Corbicula fluminea*	<0.5-7.2[x]	<0.5[x]	18-40[x]	NA	NA	NA	Pereira et al. 1996
Guanabara Bay, Brazil	1996	*Perna perna*	NA	0.54-14.9[x]	NA	NA	NA	NA	De Brito et al. 2002
Monterey Harbour, California, USA	1999	Mussel	NA	0.96[z]	2.23[z]	0.1[z]	NA	NA	Kannan et al. 2004
Salton Sea Lake, CA, USA	2001	*Tilapia mossambique*	0.3-11.4[z]	0.4-54.9[z]	NA	NA	NA	NA	Sapozhinkova et al. 2004
2- Fish along the Egyptian Coast									
Mediterranean Sea, Port Said, Egypt	1983	*Solea vulgaris*	NA	NA	0.1-39.2[x]	NA	NA	NA	EL-Dib and Badawy, 1985
Abu Qir Bay	1985	*Pagellus erythrinus*	NA	5.2-7.4[z]	NA	3.2-4.8[z]	NA	NA	EL-Nabawi et al. 1987b
		Sargus vulgaris	NA	4.6-7.9[z]	NA	3.3-8.4[z]	NA	NA	
		Siganus rivulatus	NA	3.9-6.4[z]	NA	6.4-8.6[z]	NA	NA	
		Sphyraena sphyraena	NA	7.8-11.3[z]	NA	6.8-9.2[z]	NA	NA	
		Trigla hirundo	NA	1.4-5.6[z]	NA	7.2-8.1[z]	NA	NA	

Table A32: Continued.

Location	Sampling year	Species type	Chlorpyrifos	Dieldrin	∑CHLs	Heptachlor epoxide	Methoxychlor	Mirex	Reference
Abu Qir Bay, Egypt	NA	*Mugil sephalus*	NA	ND	NA	NA	2.1[z]	1.4[z]	Abd-Allah et al. 1998
Nile River and Manzala Lake	1993	*Tilapia nilotica*	NA	NA	0.1-2.7[z]	NA	NA	NA	Yamashita et al. 2000
3- Mussels along the Egyptian Coast									
Abu Qir Bay, Egypt	NA	*Donax trunculus*	NA	0.6[z]	NA	NA	ND	2.2[z]	Abd-Allah et al. 1998

NA: Not available
ND: Not detected

Table A33: Concentrations of PAHs (µg/kg dw) in surfacial sediments of Abu Qir Bay.

Station No.	Nap	Acy	Ace	Flr	Phn	Ant	Fla	Pyr	BaA	Chy	BbF	BkF	BaP	InP	DibA	BghiP	ΣPAHs
1	16.5	21.4	25.8	51.8	59.1	52.9	122	66.0	44.2	41.6	25.7	20.8	24.1	<DL	<DL	<DL	572
2	22.5	24.6	23.3	65.5	73.7	69.7	236	103	51.0	58.7	82.9	23.7	63.3	<DL	<DL	<DL	898
3	37.4	25.8	23.4	32.1	39.6	34.4	53.1	41.9	44.2	26.0	34.2	23.6	36.0	35.3	75.3	37.1	600
4	19.9	24.6	24.9	34.9	65.0	58.7	98.1	80.7	69.9	44.9	60.8	30.6	61.4	48.1	15.7	27.8	766
5	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
8	6.05	5.97	<DL	9.75	24.4	12.0	45.5	33.1	27.3	21.0	30.4	13.2	25.2	12.6	4.33	18.1	289
9	4.18	4.91	4.04	6.21	5.78	7.07	3.93	4.76	3.10	4.21	5.92	4.56	4.44	3.34	<DL	2.65	69.1
12	6.26	8.54	6.98	9.77	8.83	11.5	10.0	7.61	9.82	7.25	8.71	7.61	8.59	11.1	3.40	6.84	133
13	9.35	9.45	8.48	12.8	12.0	13.5	14.4	8.24	11.0	8.26	11.9	9.34	10.5	11.9	31.7	14.9	198
14	13.0	11.7	12.8	21.5	66.0	30.9	149	107	78.8	61.5	109	23.0	230	6.57	5.03	4.69	930
15	14.8	5.68	4.86	7.65	13.7	10.1	35.3	21.5	16.3	11.7	17.6	6.05	18.0	7.40	3.38	11.6	206
18	6.09	5.75	5.30	11.0	11.3	7.55	8.88	10.5	9.38	6.68	8.05	5.08	6.42	4.11	<DL	2.85	109
19	17.1	13.0	12.6	<DL	27.2	17.3	45.9	34.2	27.1	19.6	27.7	14.3	24.7	27.4	14.4	20.0	343
20	6.58	16.5	8.50	34.5	52.7	43.1	177	277	54.8	26.8	72.6	36.7	18.1	<DL	<DL	<DL	825
21	<DL	25.4	20.5	51.7	60.1	49.9	98.9	54.6	42.6	37.9	33.1	23.9	48.5	<DL	<DL	<DL	547
22	<DL	4.21	<DL	6.93	7.52	6.23	12.5	6.67	8.15	7.40	9.07	6.98	6.24	3.94	8.31	<DL	94.1
23	22.9	5.41	<DL	10.9	36.6	11.5	55.5	36.9	31.0	20.1	31.9	11.2	24.8	11.9	9.03	8.07	331
25	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
26	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
27	5.17	20.1	35.6	496	470	211	357	490	185	297	28.3	35.9	29.8	<DL	<DL	<DL	2660
Min	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**
Max	**37.4**	**25.8**	**35.6**	**496**	**470**	**211**	**357**	**490**	**185**	**297**	**109**	**36.7**	**230**	**48.1**	**75.3**	**37.1**	**2660**
Mean	**10.4**	**11.7**	**10.8**	**43.1**	**51.7**	**32.4**	**76.2**	**69.1**	**35.7**	**35.0**	**29.9**	**14.8**	**32.0**	**9.19**	**8.53**	**7.73**	**478**
Sd	**10.0**	**9.12**	**11.0**	**108**	**102**	**47.2**	**93.7**	**118**	**42.4**	**64.5**	**29.9**	**11.7**	**50.2**	**13.3**	**17.6**	**10.7**	**601**

<DL = below the limit of detection

Table A34: Molecular ratios of PAHs in surfacial sediments of Abu Qir Bay.

Sample No.	$\Sigma PAHs_{combust}$	$\Sigma PAHs_{toxic}$	Phn/Ant	Fla/Pyr	Ant/Ant+Phn	Fla/Fla+Pyr	BaA/BaA+Chy	InP/InP+BghiP
1	321	156	1.12	1.85	0.472	0.649	0.515	ND
2	556	280	1.06	2.30	0.486	0.697	0.465	ND
3	371	275	1.15	1.27	0.465	0.559	0.630	0.488
4	477	331	1.11	1.22	0.474	0.549	0.609	0.634
5	<DL	<DL	ND	ND	ND	ND	ND	ND
8	206	134	2.03	1.37	0.330	0.579	0.565	0.411
9	32.5	25.6	0.818	0.826	0.550	0.452	0.424	0.558
12	72.4	56.5	0.769	1.32	0.565	0.569	0.575	0.620
13	122	94.6	0.887	1.74	0.530	0.635	0.572	0.443
14	544	514	2.13	1.40	0.319	0.583	0.562	0.583
15	131	80.5	1.36	1.64	0.424	0.621	0.581	0.390
18	55.5	39.7	1.49	0.848	0.401	0.459	0.584	0.590
19	231	155	1.57	1.34	0.389	0.573	0.581	0.578
20	645	209	1.22	0.641	0.450	0.391	0.672	ND
21	291	186	1.21	1.81	0.453	0.644	0.529	ND
22	63.0	50.1	1.21	1.87	0.453	0.652	0.524	1.00
23	216	140	3.18	1.50	0.239	0.601	0.607	0.595
25	<DL	<DL	ND	ND	ND	ND	ND	ND
26	<DL	<DL	ND	ND	ND	ND	ND	ND
27	1392	576	2.23	0.728	0.310	0.421	0.384	ND
Min.	**32.5**	**25.6**	**0.769**	**0.641**	**0.239**	**0.391**	**0.384**	**0.390**
Max.	**1392**	**576**	**3.18**	**2.30**	**0.565**	**0.697**	**0.672**	**1.00**
Mean	**286**	**165**	**1.23**	**1.18**	**0.366**	**0.482**	**0.469**	**0.344**
Sd.	**329**	**162**	**0.780**	**0.659**	**0.178**	**0.223**	**0.213**	**0.313**

ND: not detected

Table A35: Concentrations of PAHs (µg/kg dw) in mussel tissues of Abu Qir Bay.

Station No.	Nap	Acy	Ace	Flr	Phn	Ant	Fla	Pyr	BaA	Chy	BbF	BkF	BaP	InP	DibA	BghiP	ΣPAHs
	Mactra corallina																
4	120	110	102	147	216	141	313	277	211	181	224	113	200	195	119	159	2827
8	64.6	35.0	33.3	44.4	59.4	45.3	97.0	93.8	58.9	61.5	88.9	57.3	72.4	82.5	48.0	71.6	1014
9	14.5	17.9	15.7	22.7	26.4	23.1	33.8	31.4	24.5	28.5	28.9	25.1	29.1	36.7	27.5	32.9	418
12	9.75	11.9	12.6	11.9	12.6	15.3	16.4	17.5	13.9	16.2	17.8	17.6	16.1	19.6	16.5	16.4	242
13	20.8	18.8	18.9	23.7	39.2	27.7	40.1	52.0	34.0	44.4	39.2	30.8	34.1	42.0	31.3	36.5	534
18	45.3	40.4	40.6	54.4	83.3	57.0	126	118	95.4	94.8	102	73.2	87.2	94.6	60.6	84.0	1257
19	17.8	20.4	22.1	34.4	84.7	42.3	157	133	93.1	104	113	63.9	95.3	91.3	45.9	79.4	1197
Min	**9.75**	**11.9**	**12.6**	**11.9**	**12.6**	**15.3**	**16.4**	**17.5**	**13.9**	**16.2**	**17.8**	**17.6**	**16.1**	**19.6**	**16.5**	**16.4**	**242**
Max	**120**	**110**	**102**	**147**	**216**	**141**	**313**	**277**	**211**	**181**	**224**	**113**	**200**	**195**	**119**	**159**	**2827**
Mean	**41.8**	**36.3**	**35.0**	**48.3**	**74.6**	**50.3**	**112**	**103**	**75.9**	**75.8**	**87.7**	**54.3**	**76.3**	**80.2**	**49.8**	**68.6**	**1070**
Sd	**39.5**	**33.9**	**31.1**	**45.7**	**68.2**	**42.6**	**103**	**88.1**	**67.7**	**56.7**	**70.9**	**33.2**	**62.5**	**58.5**	**33.7**	**47.7**	**870**
	Tapes decussata																
25	<DL	<DL	<DL	<DL	<DL	<DL	11.4	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	11.4
26	<DL	<DL	9.46	<DL	<DL	<DL	12.1	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	21.6
27	48.9	51.1	62.4	135	289	173	471	440	304	343	363	223	300	291	146	236	3875
Min	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**11.4**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**<DL**	**11.4**
Max	**48.9**	**51.1**	**62.4**	**135**	**289**	**173**	**471**	**440**	**304**	**343**	**363**	**223**	**300**	**291**	**146**	**236**	**3875**
Mean	**16.3**	**17.0**	**24.0**	**45.0**	**96.2**	**57.7**	**165**	**147**	**101**	**114**	**121**	**74.3**	**103**	**96.8**	**48.8**	**78.5**	**1303**
Sd	**28.2**	**29.5**	**33.6**	**78.0**	**167**	**99.9**	**265**	**254**	**175**	**198**	**209**	**129**	**171**	**168**	**84.5**	**136**	**2228**

<DL = below the limit of detection

Table A36: Molecular ratios of PAHs in the mussel tissues of Abu Qir Bay.

Sample No.	Phn/Ant	Fla/Pyr	Ant/Ant+Phn	Fla/Fla+Pyr	BaA/BaA+Chy	InP/InP+BghiP
4	1.53	1.13	0.395	0.531	0.538	0.550
8	1.31	1.03	0.433	0.509	0.489	0.535
9	1.14	1.08	0.467	0.518	0.462	0.527
12	0.826	0.935	0.548	0.483	0.463	0.544
13	1.42	0.771	0.414	0.435	0.434	0.535
18	1.46	1.06	0.406	0.515	0.502	0.530
19	2.00	1.17	0.333	0.540	0.473	0.535
25	ND	ND	ND	1.00	ND	ND
26	ND	ND	ND	1.00	ND	ND
27	1.67	1.07	0.375	0.517	0.470	0.552
Min.	**0.589**	**0.771**	**0.333**	**0.435**	**0.233**	**0.00**
Max.	**2.00**	**1.76**	**0.629**	**1.00**	**0.538**	**0.552**
Mean	**1.14**	**0.830**	**0.337**	**0.605**	**0.383**	**0.431**
Sd.	**0.673**	**0.449**	**0.186**	**0.210**	**0.204**	**0.227**

ND: not detected

Table A37: Concentrations of PAHs (µg/kg dw) in sediments worldwide.

Location	Sampling year	∑PAHs (sediments)	Reference
Abu Qir Bay	2006	<DL-2660 (478)	Present study
1- Sediments worldwide			
Corsica, Italy	1987	3.9-53.5	Narbone et al. 1991
Touloun, France		912-8533	
Casco Bay, USA	NA	16-21000	Kennicut et al. 1994
San Joaquin River, California	1992	12-780	Pereira et al. 1996
San Diego Bay, USA	NA	80-20000	Anderson et al. 1996
Mediterranean Sea	1985-1986	20-960	Yilmaz et al. 1998
	1995	680-4800	
	1996	550-18700	
Kyeonggi Bay, Korea	1995	9.1-1400	Kim et al. 1999
Arcachon Bay, France	1995	31.7-2390	Baumard et al. 1999
French Coast, Mediterranean Sea	1995	1.47-20400	
Bohia and Yellow Sea, China	NA	20.4-5734	Ma et al. 2001
Catalonia Coast, Spain	2001	13.4-16700	Eljarrat et al. 2001
Izimut Bay, Turkey	1999	30-1670	Telli-Karakoc et al. 2002
Cork Harbour, Ireland	NA	528-2878	Kilemade et al. 2004
San Francisco Bay, USA	2001	18-2231	Oros et al. 2007
Inner Clyde Estuary, UK	2003	630-23711	Vane et al. 2007
2- Alexandria Coast			
EL-Mex Bay, Egypt	NA	1200000-7300000	Abd-Allah and EL-Sebae, 1995
Western Harbour	1999	7.9-131149	Mostafa et al. 2003
Abu Qir Bay, Egypt	2004	94.9-1448	EL-Deeb et al. 2007
Western Harbour	1999	1999	EL-Nemr et al. 2007
Eastern Harbour		6338	
EL-Mex Bay, Egypt		4326	

NA: Not available

Table A38: Concentrations of PAHs (µg/kg) in different species worldwide.

Location	Sampling year	Species type	∑PAHs	Reference
Abu Qir Bay, Egypt	2006	*Mactra corallina*	242-2827[x] (1070)	Present study
			5957-54690[y] (22136)	
			44.5-526[z] (200)	
		Tapes decussata	55.0-3875[x] (1329)	
			672-43883[y] (15087)	
			10.3-701[z] (241)	
1- Mussels worldwide				
Catalonia	NA	*Mytilus galloprovincialis*	670-5491[z]	Porte and Albaiges, 1994
San Joaquin River, California	1992	*Corbicula fluminea*	14-74[x]	Pereira et al. 1996
Arcachon Bay, France	1995	*Mytilus galloprovincialis*	279-2420[x]	Baumard et al. 1999
French coast, Mediterranean Sea	1995	*Mytilus galloprovincialis*	25.6-373[x]	
Ebro Delta, NW Mediterranean	1989-1991	*Mytilus galloprovincialis*	70-150[z]	Sole et al. 2000
		Ostrea edulis	10-220[z]	
		Crassostrea gigas	20-50[z]	
		Rotala decussata	20-120[z]	
Haifa Bay	1995-1998	*Mactra corallina*	54-267[x]	Zimand , 2002
Bay of Fundy, Atlantic Canada	1996-1998	*Mytilus edulis*	ND-248[x]	Chou et al. 2003
Baltic Sea, Poland	1997	*Mytilus edulis*	8.64-29.7[z]	Potrykus et al. 2003
Corral Bay, Chile	1999-2000	*Mytilus chilensis*	138-876[x]	Palma-Fleming et al. 2003
Guanabara Bay, Brazil	1999	*Perna perna*	9-273[x]	Francioni et al. 2007
2- Marine species along the Egyptian Coast				
Red Sea, Egypt	2000	*Brachiodonates* sp.	676-4666[z]	EL-Nemr et al. 2003
Abu Qir Bay, Egypt	2004	*Donax trunculus*	1137[z]	EL-Deeb et al. 2007
		Peneaus japonicus	923[z]	
		Solea solea	1768[z]	

NA: Not available

Appendix II

Table A1: Correlation matrix of trace metals in sediments of Abu Qir Bay.

	Al (%)	Mn	Fe (%)	V	Cr	Co	Ni	Cu	Zn	As	Sn	Se	Cd	Hg	Pb	TOC (%)	Sand	Silt (%)	Clay (%)	Silt + clay
Al (%)	1																			
Mn	0.71	1																		
Fe (%)	0.70	0.79	1																	
V	0.56	0.80	0.85	1																
Cr	0.62	0.79	0.84	0.89	1															
Co	0.63	0.78	0.97	0.92	0.85	1														
Ni	0.62	0.80	0.88	0.97	0.87	0.94	1													
Cu	0.75	0.63	0.72	0.53	0.66	0.64	0.61	1												
Zn	0.75	0.63	0.72	0.55	0.73	0.64	0.63	0.98	1											
As	0.80	0.66	0.82	0.65	0.71	0.78	0.73	0.80	0.81	1										
Sn	-0.12	0.30	0.27	0.31	0.38	0.33	0.23	0.03	0.08	0.02	1									
Se	0.39	0.43	0.31	0.22	0.28	0.26	0.18	0.20	0.23	0.27	0.25	1								
Cd	0.86	0.73	0.71	0.57	0.65	0.68	0.61	0.71	0.72	0.87	0.02	0.46	1							
Hg	0.58	0.73	0.68	0.54	0.57	0.68	0.63	0.74	0.71	0.67	0.21	0.24	0.67	1						
Pb	0.72	0.82	0.90	0.93	0.88	0.91	0.90	0.64	0.65	0.68	0.31	0.35	0.66	0.56	1					
TOC (%)	0.61	0.38	0.37	0.23	0.26	0.30	0.30	0.78	0.69	0.53	-0.13	-0.02	0.47	0.49	0.35	1				
Sand (%)	-0.86	-0.67	-0.62	-0.52	-0.50	-0.59	-0.58	-0.58	-0.59	-0.76	0.15	-0.45	-0.89	-0.54	-0.64	-0.43	1			
Silt (%)	0.77	0.59	0.50	0.43	0.38	0.49	0.48	0.44	0.45	0.65	-0.18	0.47	0.83	0.45	0.54	0.32	-0.98	1		
Clay (%)	0.91	0.75	0.81	0.67	0.75	0.75	0.74	0.82	0.85	0.88	0.00	0.25	0.84	0.67	0.77	0.63	-0.80	0.67	1	
Silt + clay	0.86	0.67	0.62	0.52	0.50	0.59	0.58	0.58	0.59	0.76	-0.14	0.45	0.89	0.54	0.64	0.43	-1.00	0.98	0.80	1

Table A2: Correlation coefficients for the relationships between the chlorinated organic compounds and TOC and clay contents in surfacial sediments of Abu Qir Bay.

	DDTs	HCHs	Cis-epoxide	a-endosulfane	b-endosulfane	Dieldrin	Cis-chlordane	Trans-chlordane	Chlordane	Chlorpyrifos
TOC (%)	0.77	0.77	0.86	0.80	0.81	0.70	0.69	0.63	0.66	0.58
Clay (%)	0.72	0.68	0.72	0.69	0.76	0.53	0.66	0.73	0.72	0.74
	Heptachlor	**Trans-epoxide**	**Aldrin**	**Mirex**	**Methoxychlor**	**PCBz**	**HCBz**			
TOC (%)	0.54	0.32	0.32	0.28	-0.12	-0.08	-0.09			
Clay (%)	0.49	0.53	0.53	0.11	0.08	0.18	0.17			

Table A3: Summary of the non-carcinogenic toxicological tests given by IRIS.

Analyte	RfD basis	RfD confidence level	RfD critical effects	RfD study species	RfD uncertainty factors	Reference
As	NOAEL	Medium	Hyperpigmentation, Keratosis and possible vascular complications	Human	3	Tseng, 1977
Cd	NOAEL	High	Significant Proteinuria	Human	10	USEPA, 1985
Cr	NOAEL	Low	Not reported	Rat	100	Ivankovic and Preussman, 1975
Hg	$BMDL_5$	High	Development of neuropsychological impairment	Human	10	Budtz-Jorgensen *et al*., 1999
Mn	NOAEL	Medium	CNS effects	Human	1	NRC, 1989
Se	NOAEL	High	Clinical selenosis	Human	3	Yang *et al*., 1989
Zn	LOAEL	Medium/high	Decrease in erythrocyte Cu, Zn-superoxide dismutase activity in healthy adults	Human	3	Milne *et al*., 2001
Nap	NOAEL	Low	Decrease mean terminal body weight in males	Rat	3000	BCL, 1980
Ace	NOAEL	Low	Hepatotoxicity	Mice	3000	USEPA, 1989
Flr	NOAEL	Low	Decreased red blood cells	Mice	3000	USEPA, 1989
Ant	NOEL	Low	No observed effects	Mice	3000	USEPA, 1989
Fla	NOAEL	Low	Hematological alterations, increase in the liver weight	Mice	3000	USEPA, 1989

NOAEL: No observed adverse effect level
$BMDL_5$: Benchmark dose 05
LOAEL: Low observed adverse effect level

Table A3: Continued.

Analyte	RfD basis	RfD confidence level	RfD critical effects	RfD study species	RfD uncertainty factors	Reference
Pyr	NOAEL	Low	Kidney effects	Mice	3000	USEPA, 1989
Lindane	NOAEL	Medium	Liver and kidney toxicity	Rat	1000	Zoecon Corp, 1983
Heptachlor	NOEL	Low	Liver weight increase	Rat	300	Velsicol Chemical, 1955
Heptachlor epoxide	LEL	Low	Increase in liver weight	Dogs	1000	Dow Chemical Co., 1958
Aldrin	LOAEL	Medium	Liver toxicity	Rat	1000	Fitzhung *et al*., 1964
Dieldrin	NOAEL	Medium	Liver lesions	Rat	100	Walker *et al*., 1969
Chlordane	NOAEL	Medium	Hepatic necrosis	Mice	300	Khasawinah and Grutsch, 1989
Endosulfane	NOAEL	Medium	Reduced body weight gain and progressive glomerulonephrosis	Rat	100	Hoechst Celanese Corp., 1989
p,p´-DDT	NOEL	Medium	Liver lesions	Rat	100	Laug *et al*., 1950
Methoxychlor	NOEL	Low	Excessive loss of litters	Rabbits	1000	Kincaid Enterprises, 1986
Mirex	NOAEL	High	Liver cytomegaly, thyroid cystic follicles	Rat	300	NTP, 1990
Chlorpyrifos	NOEL	Medium	Decreased plasma ChE activity	Humans	10	Dow chemicals, 1972
HCBz	NOAEL	Medium	Liver effects	Rat	100	Arnold *et al*., 1985
PCBz	LOAEL	Low	Liver and kidney toxicity	Rat	10000	Linder *et al*., 1980

LEL: least effect level
NOEL: No observed effect level

Table A4: Summary of the carcinogenic toxicological tests given by IRIS.

Element	EPA cancer class	Oral study species	Oral target organ and effect	Reference
As	A	Human	Skin	USEPA, 1987
BaP	B2	Mice	Forestomach carcinomas	Brune *et al*., 1981
PCBs	B2	Rats	Hepatocellular carcinomas	Brunner *et al*., 1996
α-HCH	B2	Mice	Hepatocellular carcinomas	Ito *et al*., 1973
β-HCH	C	Mice	Hepatocellular carcinomas	Thorpe and Walker, 1973
HCHs	B2	Mice	Hepatocellular carcinomas	Munir *et al*., 1983
Heptachlor	B2	Mice	Hepatocellular carcinomas	NCI, 1977
Heptachlor epoxide	B2	Mice	Hepatocellular carcinomas	Velsicol, 1973
Aldrin	B2	Mice	Liver carcinoma	NCI, 1978
Dieldrin	B2	Mice	Liver carcinoma	Meierhenry *et al*., 1983
Chlordane	B2	Mice	Hepatocellular carcinomas	NCI, 1977
p,p´-DDE	B2	Mice	Hepatocellular carcinomas	Rossi *et al*., 1983
p,p´-DDD	B2	Mice	Liver tumors	Tomatis *et al*., 1974
p,p´-DDT	B2	Mice	Liver tumors	Rossi *et al*., 1977
HCBz	B2	Rat	Hepatocellular carcinomas	Erturk *et al*., 1986

A: Human carcinogen
B2: Probable human carcinogen but data are inadequate for humans
C: Possible human carcinogen

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